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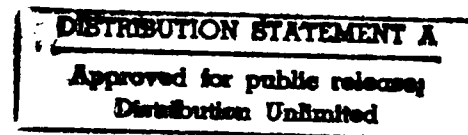


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Removal of Pollutant Compounds From Water Supplies Using  
Ozone, Ultraviolet Light, and a Counter Current Packed Column

Emery Leonard Kelly  
B.S., California State University, Sacramento, 1986

PROJECT

Submitted in partial satisfaction of the  
requirements for the degree of

MASTER OF SCIENCE

in

CIVIL ENGINEERING

at

CALIFORNIA STATE UNIVERSITY, SACRAMENTO

FALL  
1991

Removal of Pollutant Compounds From Water Supplies Using  
Ozone, Ultraviolet Light, and a Counter Current Packed Column

A Project

By

Emery Leonard Kelly

Approved by:

Kenneth D. Kerri, Chair  
Kenneth D. Kerri

Date: December 19, 1991

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Department of Civil Engineering

December 20, 1991

Date

## Abstract

of

Removal of Pollutant Compounds From Water Supplies Using  
Ozone, Ultraviolet Light, and a Counter Current Packed Column

by

Emery Leonard Kelly

### Statement of the Problem

Many water pollutants are determined to be carcinogenic and often appear in very low concentrations and still pose a health risk. Conventional water treatment processes cannot remove these contaminants and there is a great demand for the development of alternative removal technologies. The use of ozone and ultraviolet light in a counter current packed column could prove to be an effective treatment process to remove these contaminants.

### Sources of Data

This project paper was developed through professional literature and research reviews and scientific text books. The bulk of the material used to develop this paper was experimental data from experiments conducted at Michigan Technological University.

### Conclusions Reached

The treatment process of ozone and ultraviolet light in a counter current packed column promises to be an effective technology to remove pollutant compounds from water supplies.

 , Chair  
Kenneth D. Kerri

## ACKNOWLEDGEMENTS

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## CHAPTER 1

### Introduction

In recent years our water supplies have become contaminated with pollutants that standard water treatment plants are not designed to effectively remove. As much as one percent of usable groundwater in the United States may be contaminated with hazardous compounds. <sup>1</sup>

Prior to the increased awareness of this problem the goals of water treatment in the United States were disinfection and removal of tastes and odors. In 1974 it was discovered that chlorination could result in the formation of trihalomethanes (THMs). Trihalomethanes are normally a result of the residual chlorine, used for disinfection, reacting with organic compounds. This finding has led to concerns about the quantity of organic compounds in water supplies and the development of regulations establishing allowable levels.<sup>2</sup>

### Statement of the Problem

Many of these contaminants have been determined to be carcinogenic, a fact that has forced the issue into the arena of national environmental concerns. The contaminants are being found, sometimes at very low concentrations, in both ground and surface water supplies, some of which are domestic water sources. Since conventional water treatment facilities cannot effectively remove many of these contaminants, there is a great demand to develop

alternative removal methods to effectively and efficiently treat contaminated water supplies.' The need for these and other new treatment technologies is demonstrated by the Environmental Protection Agency's Superfund Innovative Technology Evaluation (SITE) Program. This program allows for new technologies to be demonstrated and evaluated for efficiency and effectiveness.' An example of a water supply becoming an Environmental Protection Agency Superfund site is the contaminated groundwater in the San Gabriel Basin. Different treatment technologies were looked at to determine possible solutions to remove the organic compound contaminants to meet drinking water standards.'

The use of ozone, ultraviolet light, and a counter current packed column could prove to be an effective and efficient treatment process to remove contaminants from water supplies.

#### Definitions of Pollutant Compounds and Advanced Oxidation

Two organic compounds that are of particular interest are trichloroethylene (TCE) and toluene. These are both listed by EPA as priority pollutants and are commonly found pollutants in contaminated groundwaters.'

The trichloroethylene is an unsaturated aliphatic halocarbon. The molecule is comprised of three chloride atoms, two carbon atoms and one hydrogen,  $\text{Cl}_2\text{C}=\text{CHCl}$ , with a

double bond between the carbons. Trichloroethylene is generally associated with degreasing solvents which is a concern in large maintenance environments, such as aircraft maintenance facilities.'

The toluene is an aromatic hydrocarbon. The molecule is comprised of seven carbon atoms and eight hydrogen atoms,  $C_6H_5-CH_3$ . Toluene has been found to be the third most frequently found chemical at superfund sites and is most commonly associated with gasoline contamination. Toluene has been found to have significant health effects.'

The development of new technologies to remove organic compounds from water supplies resulted in the consideration of oxidation processes. Oxidation processes are of interest because they completely destroy the compounds by breaking them down to nontoxic ions, carbon dioxide, and water.' Chemical oxidation appears to be an attractive and effective method of treating water supplies however, some rate constants for certain compounds have been found to be low enough to make retention times for chemical oxidation not practical for large scale operations.

There is now a growing interest in the study and development of a newer technology commonly known as enhanced or advanced oxidation processes (AOPs). Advanced oxidation processes are a combination of a chemical oxidation process, such as hydrogen peroxide ( $H_2O_2$ ) or ozone ( $O_3$ ), with a catalyst, such as ultraviolet light

(UV). This process involves the decomposition of ozone which in turn leads to the generation of hydroxyl radicals ( $\text{OH}^\cdot$ ). These hydroxyl radicals, or intermediates, are highly reactive and enhance the reaction rate to the order of several magnitudes higher, relative to using the chemical oxidant alone."

The objective of the study is to investigate the use of ozone alone and combined with ultraviolet light to remove pollutant compounds, trichloroethylene and toluene, from water in a counter current packed column. Salicylic acid will also be evaluated as it is a good indicator for the processes removal of carbon compounds. All the above compounds will be experimented with using initial concentrations of 1 and 10 mg/l.

The resulting data will be analyzed using gas chromatography and mass balance equations. The effluent concentration of chloride ions will be used in determining the amount of chlorinated hydrocarbons destroyed by the oxidation of trichloroethylene. The data will be presented in the form of charting a given ozone concentration, with and without ultraviolet light, on a chart of volumetric air/water (G/L) flow ratios vs. percent contaminant removed.

## CHAPTER 2

### Ozone Treatment

Ozone has been used as an oxidating agent for over eighty years. It is known as one of the most powerful oxidants available. Ozone has the potential to oxidize many organic compounds to carbon dioxide and water. However, in practice ozone appears to be quite selective in the oxidation of organic compounds.<sup>11</sup>

The reaction between ozone and organic compounds is two fold. The first is a direct reaction between the compound and ozone. It is this portion that is substrate selective and fairly slow. The second mechanism for oxidation is through the formation of hydroxyl radicals. Hydroxyl radicals are non-selective and much faster, on the order of five to seven magnitudes higher than the direct reaction. The chemistry of the reactions of ozone in an aqueous solution is very complex consisting of many cyclic and linear reactions. The studies of these reactions are still not conclusive as to the exact chemistry that takes place. It is not the intent of this paper to try and determine the exact chemistry.<sup>12</sup>

The reaction involving the hydroxyl radicals is a chain type reaction that can be promoted or terminated depending on the composition of the water being treated. For example if the water contains bicarbonate or humic material the chain will be terminated. This is a result of



the bicarbonate and humic material acting as hydroxyl scavengers and competing with the contaminant. There are other instances where there will be promoters in the water and the chain reaction will take place without any assistance from a catalyst such as hydrogen peroxide or ultraviolet light. When these promoters are absent then the reaction rates for ozone may not be fast enough to make the process practical. This is where a catalyst such as ultraviolet light can enhance the process enough to make it a feasible treatment method."

#### Ultraviolet Light Treatment

The use of ultraviolet light for treatment alone has generated much interest in the field of treating contaminated groundwater. It is currently applied to remove unsaturated hydrocarbons such as trichloroethylene and tetrachloroethylene. The reaction that allows ultraviolet light to destroy these compounds is fairly simple. The energy put out from the ultraviolet radiation is in the 253.7 nanometer range which happens to be the necessary wavelength to be absorbed and destroy the carbon bonds for some contaminants, such as trichloroethylene. The energy causes the bond to shatter and destroy the contaminant, reducing it into carbon dioxide, chloride ion, and water. This chloride ion does have the potential to convert into hydrochloric acid (HCl). However, this usually results in such dilute concentrations that any

resulting change in pH is not a concern.

Ozone and Ultraviolet Light Treatment.

One of the promising technologies to treat contaminated water supply sources is the combination of ozone and ultra-violet light. The use of these two treatment technologies is called an advanced oxidation process. It is described as an advanced process because the reaction rates for the two treatments are enhanced by several magnitudes when combined. It has been demonstrated that using ultraviolet light as a photo catalyst for ozone will result in most compounds more readily destroyed than with either process alone. There seem to be two distinct advantages to using ultraviolet light and ozone processes. The first is that the ultraviolet light has the capability for direct photolysis of many compounds and secondly the combined process seems to be self regulating. This infers that the process will generate needed hydroxyl radicals to enhance any direct reactions that may take place.<sup>14,15</sup>

## CHAPTER 3

### Experimental Procedure and Apparatus

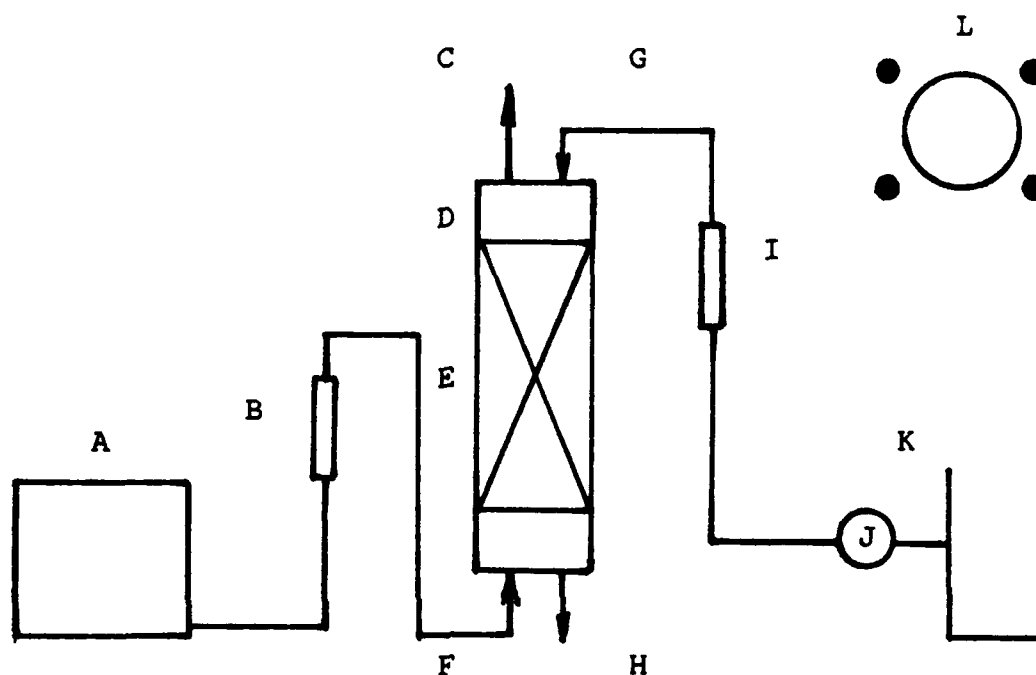
The experimental procedure was to initiate a flow of contaminated water entering the top of the packed column and flowing through the column discharging out of the bottom. At the same time, a flow of air, containing ozone, was injected into the column through a sparger located at the bottom. The air was forced through the column in the opposite direction of the liquid (counter current) and vented from the top of the column, see Figure 1.

The column is three foot by four inch diameter and made out of pyrex glass. The packing material used was 3/8 inch glass Raschig rings. The column was randomly packed with Raschig rings to a height of twenty-eight inches.

The ozone was generated using a Welshach Laboratory Ozonator, Model T-816. The air supply to the ozone generator was compressed breathing air. This was used to reduce the moisture and oils normally found in ambient air conditions from entering the ozone generator. The required air needed to ensure the desired flow rate was made-up using compressed house air. This make-up air was introduced at the effluent point of the ozone generator.

The ultraviolet light radiation was supplied using four ultraviolet blacklight bulbs, each 40 watts, 48 inches in length and emitting wavelengths of approximately 310 nanometers. The lights were placed approximately 1 1/2

Figure 1  
Experimental Aparatus



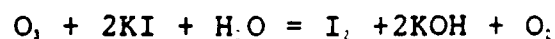
A. Ozone Generator  
B. Air Flow Rotameter  
C. Air Flow Effluent  
D. Column  
E. Raschig Packing  
F. Air Flow Influent

G. Water Flow Influent  
H. Water Flow Effluent  
I. Water Flow Rotameter  
J. Pump  
K. Water Feed Tank  
L. Ultraviolet Lights

inches around the outside of the column. The entire setup was wrapped in white poster board to reflect as much light as possible back into the system and provide protection to personnel, see Figure 1.

The contaminated water was made using a batch mix in a large carboy with a volume of approximately twelve gallons. Two carboys were used as feed tanks for the system. The contaminants were evaluated at two initial feed concentrations of approximately 1 and 10 mg/l. The water flow rate was controlled using a water pump and a liquid flow rotameter. The flow rate was varied to obtain three volumetric air/water flow ratios of one, five, and ten.

The ozone concentration was determined using a generated calibration curve. The calibration curve was developed by determining different ozone mass flow rates for five different voltage settings. The mass of ozone was determined by passing a known volume of ozonated air from the ozone generator through a 2 percent solution of neutral potassium iodide (KI). The solution was then acidified using 1 molar sulfuric acid and then titrated with standardized 0.1 normal sodium thiosulfate using starch as an indicator. The following reaction takes place:



The concentration in ozone was then calculated and converted into mg/min.<sup>14</sup> Each voltage setting was plotted as a curve of air flow rate (l/min) vs. ozone mass flow

rate (mg/min) as shown in Figure 2. The calibration curve was used to obtain three mass flow rates of 1, 3, and 5 mg/l of ozone per liter of air. The total air flow rate was controlled with an air flow rotameter. The flow rate was varied in order to obtain the desired volumetric air/water flow rates and ozone concentrations. Tables 1 and 2, indicate the different experimental conditions that were evaluated; volumetric air/water flow rates, ozone concentrations, and contaminant concentrations.

#### Data Collection

The concentration of initial feed solutions were sampled directly from the center of the large carboys. The samples were taken with a large clean glass syringe with a long stainless steel needle attached. The extracted solution was then injected into two supelco sample vials for analysis using gas chromatography.

The contaminated water effluent samples for each experimental condition were collected in a clean glass flask and then transferred into supelco sample vials to be analyzed by gas chromatography. Each sample was taken after near steady state conditions were reached. The lack of a larger volume feed tank was a time limiting factor.

The collection of samples for chloride ion analysis was conducted identical to the contaminated water effluent. Chloride ion samples were only taken for the trichloro-ethylene contaminant to be analyzed by ion chromatography.

**Figure 2**  
**Ozone Calibration Curves**

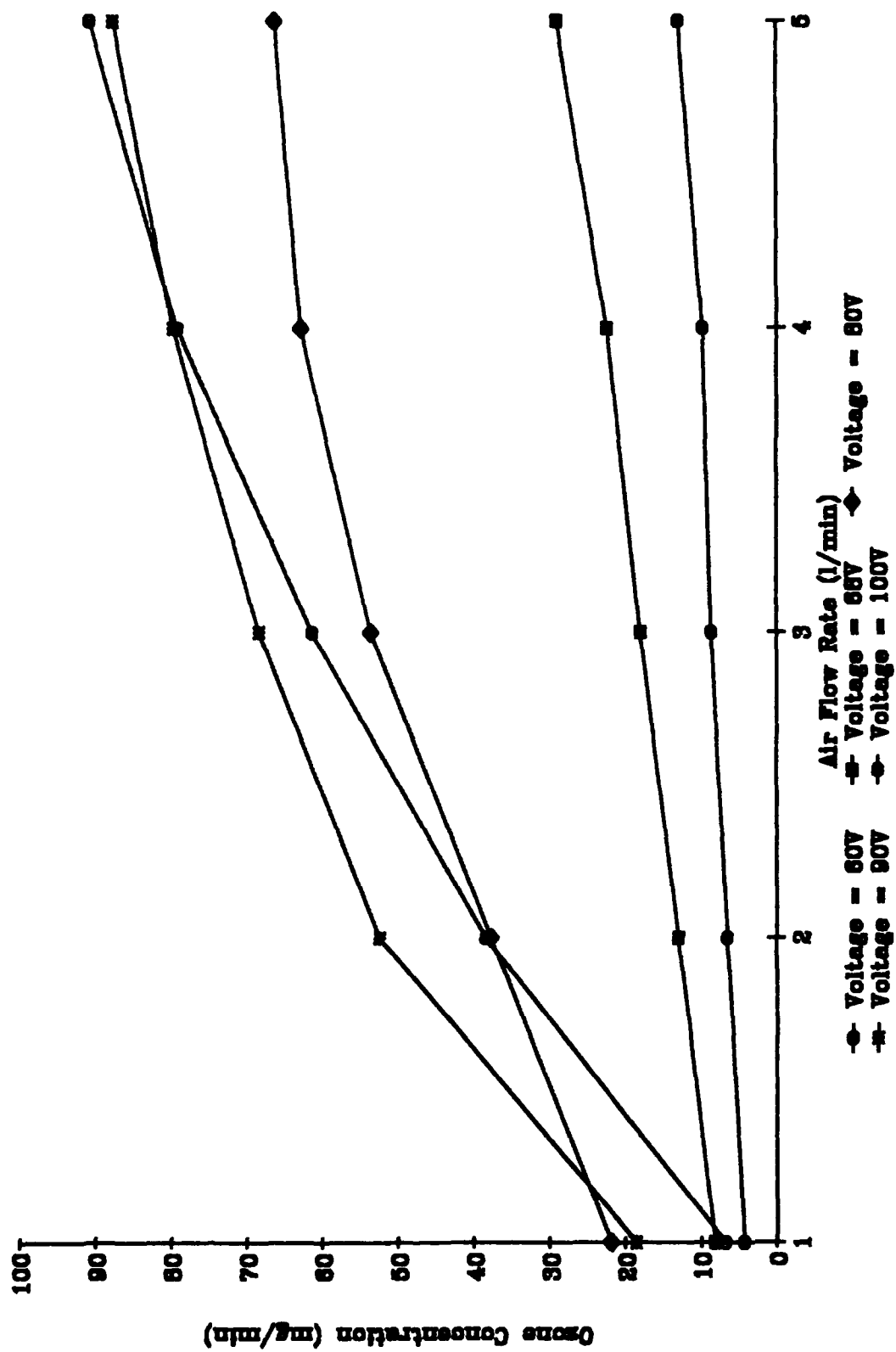


Table 1Experimental Conditions

<u>TCE, 1 mg/l</u>			<u>TCE, 10 mg/l</u>			<u>Toluene, 1 mg/l</u>		
<u>G/L</u>	<u>O,</u>	<u>UV</u>	<u>G/L</u>	<u>O,</u>	<u>UV</u>	<u>G/L</u>	<u>O,</u>	<u>UV</u>
1	0		1	0		1	0	
5	0		5	0		5	0	
10	0		10	0		10	0	
20	0		20	0		20	0	
1	1		1	1		1	1	
5	1		5	1		5	1	
10	1		10	1		10	1	
20	1		20	1		20	1	
1	1	X	1	1	X	1	1	X
5	1	X	5	1	X	5	1	X
10	1	X	10	1	X	10	1	X
20	1	X	20	1	X	20	1	X
1	3		1	3		1	3	
5	3		5	3		5	3	
10	3		10	3		10	3	
20	3		20	3		20	3	
1	3	X	1	3	X	1	3	X
5	3	X	5	3	X	5	3	X
10	3	X	10	3	X	10	3	X
20	3	X	20	3	X	20	3	X
1	5		1	5		1	5	
5	5		5	5		5	5	
10	5		10	5		10	5	
20	5		20	5		20	5	
1	5	X	1	5	X	1	5	X
5	5	X	5	5	X	5	5	X
10	5	X	10	5	X	10	5	X
20	5	X	20	5	X	20	5	X



Table 2Experimental ConditionsSalicylic Acid, 1 mg/l

<u>G/L</u>	<u>O,</u>	<u>UV</u>
------------	-----------	-----------

1	0	
5	0	
10	0	
20	0	
1	1	
5	1	
10	1	
20	1	
1	1	X
5	1	X
10	1	X
20	1	X
1	3	
5	3	
10	3	
20	3	
1	3	X
5	3	X
10	3	X
20	3	X
1	5	
5	5	
10	5	
20	5	
1	5	X
5	5	X
10	5	X
20	5	X

Salicylic Acid, 10 mg/l

<u>G/L</u>	<u>O,</u>	<u>UV</u>
------------	-----------	-----------

1	0	
5	0	
10	0	
20	0	
1	1	
5	1	
10	1	
20	1	
1	1	X
5	1	X
10	1	X
20	1	X
1	3	
5	3	
10	3	
20	3	
1	3	X
5	3	X
10	3	X
20	3	X
1	5	
5	5	
10	5	
20	5	
1	5	X
5	5	X
10	5	X
20	5	X

## CHAPTER 4

### Sample Analysis Methods

The trichloroethylene and toluene contaminated water influent and effluent concentrations were determined using gas chromatography, Hewlett Packard Model 5880. For trichloroethylene direct injection and an electron capture detector was used to measure influent and effluent concentrations. For the toluene, purge and trap injection with a flame ionization detector was used to measure concentrations.

The salicylic acid concentrations were determined by analyzing the samples for total nonpurgable organic carbon. It was assumed that any removal due to the experimental process would be accounted for by the difference in the influent and effluent nonpurgable organic carbon concentrations.

The chloride samples were to be analyzed using an ion chromatograph measuring for the amount of chloride ion in the water effluent.

### Experimental Results

After running the experiments the samples were taken to the environmental engineering laboratory to be analyzed. Throughout the data there are some data points missing. These are the results of laboratory mistakes or equipment mishaps.

### Trichloroethylene

The first set of data analyzed was from the experiments with trichloroethylene. Again, the analysis was done with a gas chromatograph with an electron capture detector. The resulting concentrations of both the influent and the effluent are shown in Tables 3 and 4. As can be seen the two initial concentrations were not exactly 1 and 10 mg/l but averaged 1.32 mg/l and 12.89 mg/l respectively. However, they were close enough to serve the purposes of the experiment since the goal was to evaluate the percent removal.

The first analysis of the data was to plot the volumetric air/water (G/L) flow ratio vs. percent contaminate removal for the different ozone concentrations for results with and without the ultraviolet light, see Figures 3, 4, 5, and 6. A simple regression was done on each set of data points for each curve and the results are tabulated in Table 5. Also multiple regressions were done on the data from the two concentrations of trichloroethylene and on the combined data of both concentrations. These results are tabulated in Table 6.

The chloride samples were lost due to laboratory error, thus no direct measurement of the amount of chloride ion in the effluent was able to be accomplished. The chloride ion would have indicated the amount of trichloroethylene that was destroyed by reacting with the

Table 3

Percent Removal of Trichloroethylene,  
Average Initial Concentration 1.32 mg/l

<u>G/L</u> <u>Ratio</u>	<u>Ozone</u> <u>(mg/l)</u>	<u>UV</u> <u>Light</u>	<u>Influent</u> <u>Conc(mg/l)</u>	<u>Effluent</u> <u>Conc(mg/l)</u>	<u>Percent</u> <u>Removal</u>
1	0	NO	1.37	0.59	57.01
5	0	NO	1.37	0.31	77.62
10	0	NO	1.37	0.23	83.50
20	0	NO	1.37	0.13	90.60
1	1	NO	1.37	0.52	62.26
5	1	NO	1.37	0.29	79.16
10	1	NO	1.37	0.18	86.78
20	1	NO	1.37	0.20	85.68
1	3	NO	1.37	0.45	67.56
5	3	NO	1.37	0.22	84.28
10	3	NO	1.37	0.17	87.75
20	3	NO	1.37	0.07	94.65
1	5	NO	1.27	0.43	66.12
5	5	NO	1.27	0.27	79.09
10	5	NO	1.27	0.17	86.88
20	5	NO	1.27	0.12	90.87
1	1	YES	1.27	0.28	77.71
5	1	YES	1.27	0.32	75.18
10	1	YES	1.27	0.21	83.34
20	1	YES	1.27	0.15	88.48
1	3	YES	1.27	0.28	77.73
5	3	YES	1.27	0.18	85.82
10	3	YES	1.27	0.19	84.92
20	3	YES	1.27	0.12	90.91
1	5	YES	1.27	0.26	79.25
5	5	YES	1.27	0.24	81.11
10	5	YES	1.27	0.13	90.08
20	5	YES	1.27	0.08	93.71

Table 4

Percent Removal of Trichloroethylene,  
Average Initial Concentration 12.89 mg/l

<u>G/L</u> <u>Ratio</u>	<u>Ozone</u> <u>(mg/l)</u>	<u>UV</u> <u>Light</u>	<u>Influent</u> <u>Conc(mg/l)</u>	<u>Effluent</u> <u>Conc(mg/l)</u>	<u>Percent</u> <u>Removal</u>
1	0	NO	12.14	5.65	53.43
5	0	NO	12.14	2.90	76.15
10	0	NO	12.14	2.40	80.25
20	0	NO	12.14	1.77	85.40
1	1	NO	12.14	5.12	57.79
5	1	NO	12.14	3.30	72.84
10	1	NO	12.14	2.20	81.87
20	1	NO	12.14	1.24	89.78
1	3	NO	12.14	4.43	63.54
5	3	NO	12.14	2.88	76.26
10	3	NO	12.14	1.69	86.10
20	3	NO	12.14	1.17	90.32
1	5	NO	12.14	2.85	76.54
5	5	NO	12.14	2.19	81.94
10	5	NO	12.14	1.91	84.28
20	5	NO	13.64	1.65	87.90
1	1	YES	13.64	4.87	64.32
5	1	YES	13.64	3.13	77.03
10	1	YES	13.64	1.94	85.75
20	1	YES	13.64	1.66	87.82
1	3	YES	13.64	5.11	62.53
5	3	YES	13.64	4.26	68.77
10	3	YES	13.64	2.28	83.26
20	3	YES	13.64	1.38	89.85
1	5	YES	13.64	4.08	70.12
5	5	YES	13.64	2.59	81.02
10	5	YES	13.64	1.46	89.31
20	5	YES	13.64	1.37	89.93

Figure 3  
TCE Removal, Initial Conc 1.32 mg/l

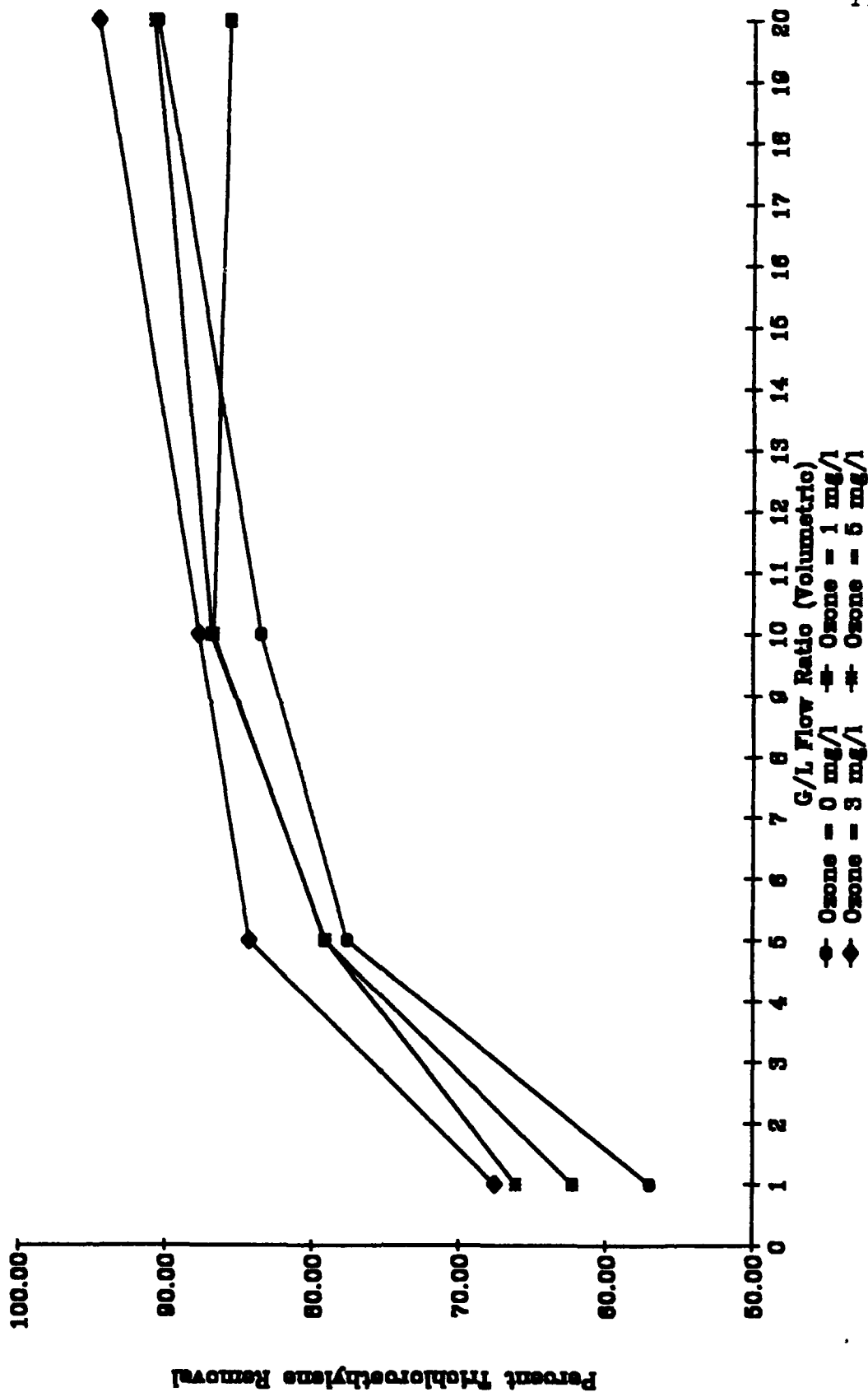


Figure 4  
TCE Removal, Initial Conc 1.32 mg/l

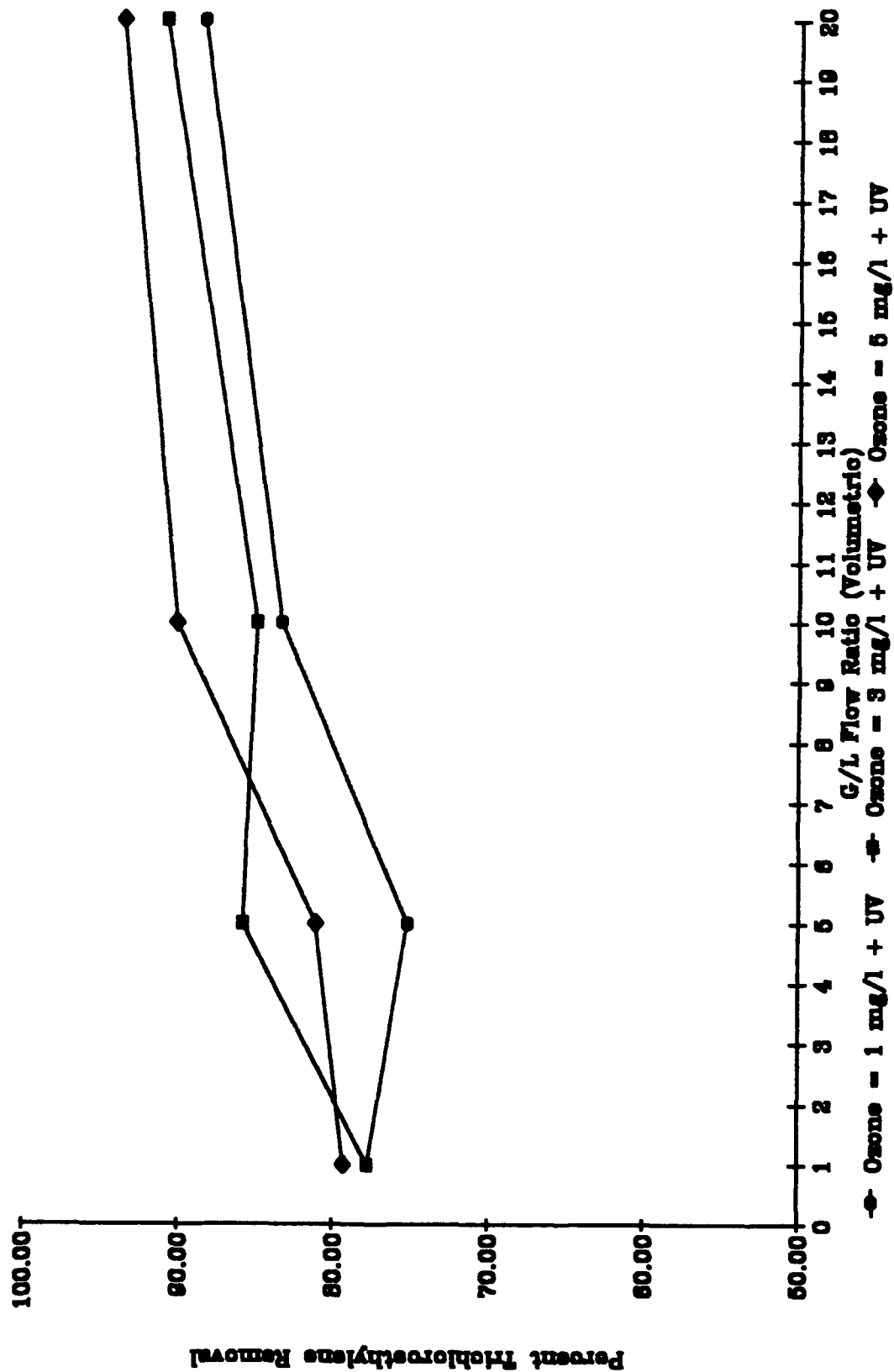


Figure 5  
TCE Removal, Initial Conc 12.88 mg/l

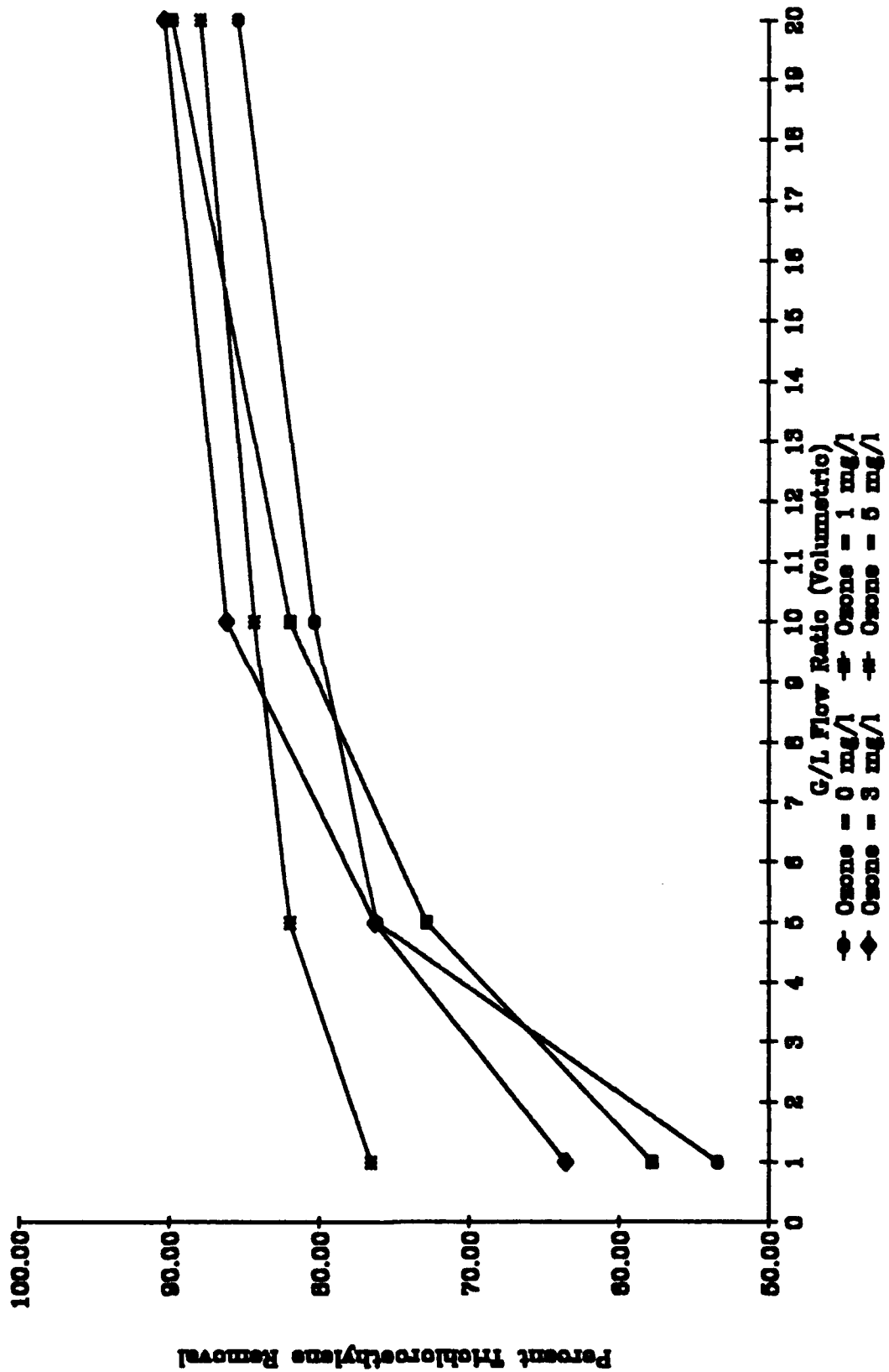




Figure 6  
TCE Removal, Initial Conc 12.89 mg/l

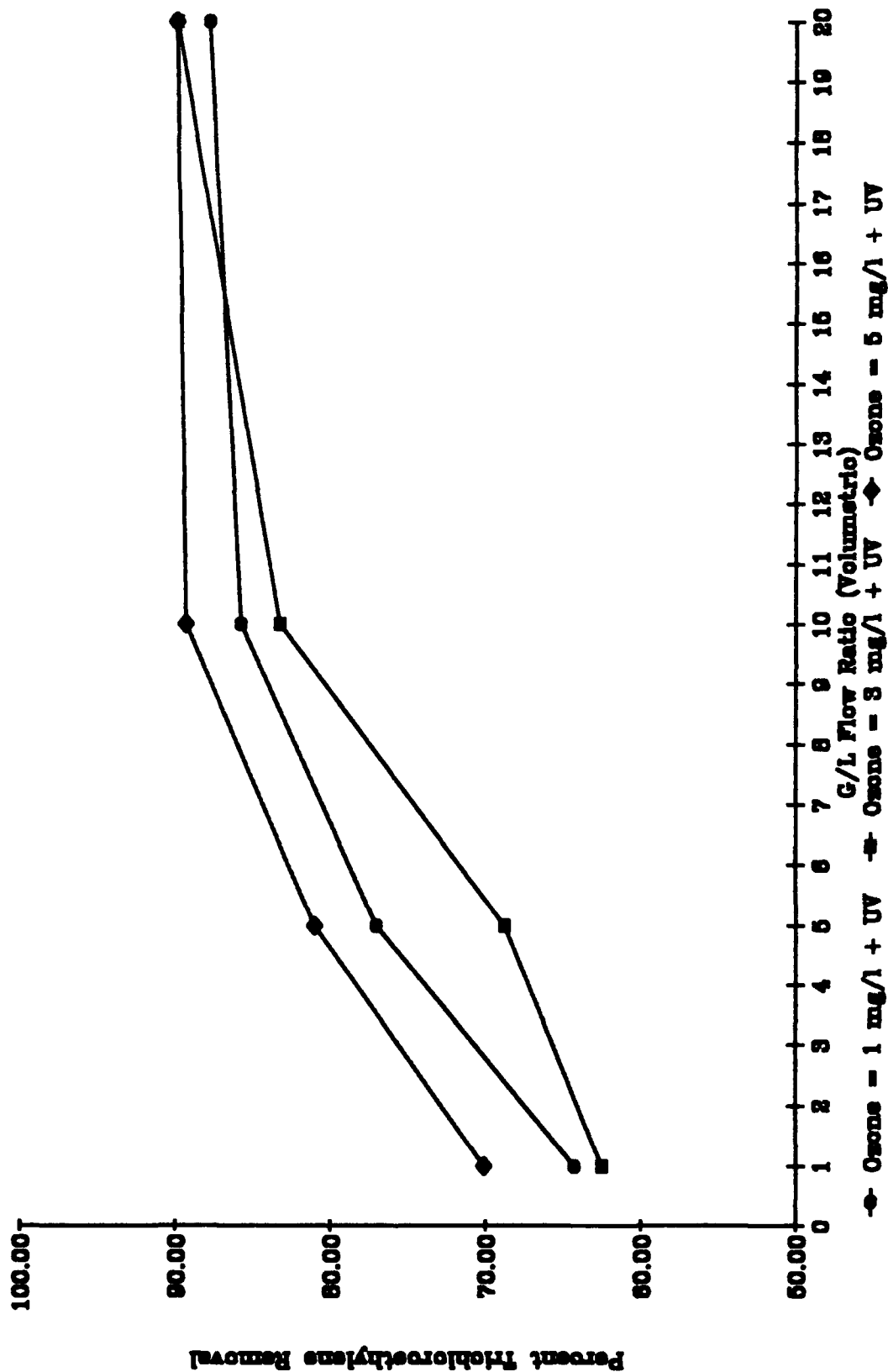


Table 5

Simple Regression Results for TCE With  
Initial Average Concentration of 1.32 mg/l

Without UV

Ozone mg/l	Comp F	Crit F*	Corr Coef	Coef of Det	Regression Equation
1	23.87	18.5	0.96	0.93	$y = 63.84 + 8.47\ln X$
3	177.24	98.5	0.99	0.99	$y = 68.12 + 8.92\ln X$
5	354.36	98.5	0.99	0.99	$y = 66.11 + 8.47\ln X$

With UV

Ozone mg/l	Comp F	Crit F	Corr Coef	Coef of Det	Regression Equation
1	10.61	18.5	0.92	0.84	$y = 75.20 + 0.66X$
3	19.93	18.5	0.95	0.91	$y = 77.88 + 4.03\ln X$
5	17.52	18.5	0.95	0.90	$y = 78.80 + 0.80X$

Initial Average Concentration of 12.89 mg/l

Without UV

Ozone mg/l	Comp F	Crit F	Corr Coef	Coef of Det	Regression Equation
1	369.21	98.5	0.99	0.99	$y = 57.14 + 10.66\ln X$
3	132.75	98.5	0.99	0.99	$y = 64.15 + 9.21\ln X$
5	190.50	98.5	0.99	0.99	$y = 76.29 + 3.69\ln X$

With UV

Ozone mg/l	Comp F	Crit F	Corr Coef	Coef of Det	Regression Equation
1	87.69	18.5	0.99	0.98	$y = 64.51 + 8.23X$
3	19.93	18.5	0.95	0.91	$y = 62.90 + 1.47\ln X$
5	47.81	18.5	0.98	0.96	$y = 70.39 + 7.07X$

\* Critical F-statistic of 18.5 for 5% level of significance and 98.5 for 1% level of significance

' Ronald E. Walpole and Raymond H Meyers, Probability and Statistics for Engineers and Scientists, 4th ed. (New York: MacMillan, 1989), 701-707.

Table 6

Multiple Regression Results for TCE With  
Initial Average Concentration of 1.32 mg/l

y = percent removal  
X1 = G/L ratio  
X2 = ozone concentration, mg/l

Without UV

Regression Equation	:	$y = 69.12 + 1.16X_1 + 0.49X_2$
Computed F-statistic	:	13.35
Critical F-statistic*	:	8.02
Computed t-statistic		
b1	:	0.48
b2	:	5.00
Critical t-statistic'		
t <sub>0.05</sub>	:	0.26
t <sub>0.01</sub>	:	2.82
Correlation Coeff.	:	0.86
Coeff. of Determination	:	0.75

With UV

Regression Equation	:	$y = 74.19 + 0.68X_1 + 1.22X_2$
Computed F-statistic	:	25.97
Critical F-statistic	:	8.02
Computed t-statistic		
b1	:	6.78
b2	:	2.72
Critical t-statistic		
t <sub>0.05</sub>	:	2.82
t <sub>0.025</sub>	:	2.26
Correlation Coeff.	:	0.92
Coeff. of Determination	:	0.85

\* Critical F-statistic of 18.5 for 5% level of significance and 98.5 for 1% level of significance

' Ronald E. Walpole and Raymond H Meyers, Probability and Statistics for Engineers and Scientists, 4th ed. (New York: MacMillan, 1989), 701-707.

Table 6 (Continued)Multiple Regression Results for TCE With  
Initial Average Concentration of 12.89 mg/l

y = percent removal  
 X1 = G/L ratio  
 X2 = ozone concentration, mg/l

Without UV

Regression Equation	:	$y = 63.48 + 1.14X_1 + 1.77X_2$
Computed F-statistic	:	15.14
Critical F-statistic*	:	8.02
Computed t-statistic		
b1	:	5.26
b2	:	1.86
Critical t-statistic <sup>†</sup>		
t <sub>1,11</sub>	:	2.82
t <sub>1,15</sub>	:	1.83
Correlation Coeff.	:	0.88
Coeff. of Determination	:	0.77

With UV

Regression Equation	:	$y = 65.57 + 1.19X_1 + 0.97X_2$
Computed F-statistic	:	14.17
Critical F-statistic	:	8.02
Computed t-statistic		
X1	:	5.31
X2	:	0.98
Critical t-statistic		
t <sub>1,11</sub>	:	2.82
t <sub>1,15</sub>	:	0.88
Correlation Coeff.	:	0.87
Coeff. of Determination	:	0.76

\* Critical F-statistic of 18.5 for 5% level of significance and 98.5 for 1% level of significance

<sup>†</sup> Ronald E. Walpole and Raymond H Meyers, Probability and Statistics for Engineers and Scientists, 4th ed. (New York: MacMillan, 1989), 701-707.

Table 6 (Continued)

Multiple Regression Results for  
Combined TCE data

y = percent removal  
 X1 = G/L ratio  
 X2 = ozone concentration, mg/l  
 X3 = TCE concentration, mg/l

Without UV

Regression Eqn :  $y = 67.27 + 1.16X_1 + 1.18X_2 - 0.18X_3$   
 Computed F-statistic: 29.09  
 Critical F-statistic\*<sup>1</sup> 4.87  
 Computed t-statistic  
     b1 : 7.48  
     b2 : 1.72  
     b3 : -0.87  
 Critical t-statistic<sup>1</sup>  
     t<sub>1,11</sub> : 2.82  
     t<sub>1,15</sub> : 1.72  
     t<sub>1,11</sub> : -0.86  
 Correlation Coef : 0.86  
 Coef of Det : 0.73

With UV

Regression Eqn :  $y = 72.82 + 0.94X_1 + 1.09X_2 - 0.39X_3$   
 Computed F-statistic: 32.48  
 Critical F-statistic: 4.87  
 Computed t-statistic  
     X1 : 7.46  
     X2 : 1.97  
     X3 : -2.80  
 Critical t-statistic  
     t<sub>1,11</sub> : 2.82  
     t<sub>1,15</sub> : 1.72  
     t<sub>1,11</sub> : -2.82  
 Correlation Coef : 0.87  
 Coef of Det : 0.76

\* Critical F-statistic of 18.5 for 5% level of significance and 98.5 for 1% level of significance

<sup>1</sup> Ronald E. Walpole and Raymond H Meyers, Probability and Statistics for Engineers and Scientists, 4th ed. (New York: MacMillan, 1989), 701-707.

ozone and/or the ultraviolet light. For every three chloride ions measured one molecule of trichloroethylene is destroyed. Since this measurement was unable to be determined the following analysis was performed.

It was assumed that the trichloroethylene was in equilibrium condition in the column. This allowed the application of Henry's Law constant to determine the amount of trichloroethylene that was stripped from the liquid phase to the gas phase. The next assumption was that the difference between the initial concentration and the amount stripped, based on Henry's Law constant, was removed by reaction with the ozone and ultraviolet light. The equation using Henry's constant is as follows:

$$C_{out} = C_{in} (1 + (H_c)(G/L)/RT)^{-1}$$

$C_{out}$  = final concentration of organic in liquid, mg/l

$C_{in}$  = initial concentration of organic in liquid, mg/l

$H_c$  = Henry's Law constant, atm·m<sup>3</sup>/mol

$G/L$  = volumetric air/water ratio

$R$  = universal gas constant, 8.206 x 10<sup>-5</sup> atm·m<sup>3</sup>/(mol·K)

$T$  = temperature, K.<sup>17</sup>

From this equation the amount of trichloroethylene was determined by subtracting the calculated final concentration from the initial concentration. Then the amount stripped was subtracted from the total amount of trichloroethylene removed by the process. The resulting amount is the quantity of trichloroethylene removed by

reaction with ozone and/or ultraviolet light. The calculated results for both trichloroethylene experiments are shown in Tables 7 and 8. In addition to the tabular representation, the results were plotted on a chart of air to water flow ratio vs. percent removal for each ozone concentration. These charts are shown in Figures 7 thru 12. A linear regression was accomplished on the data calculated by applying Henry's Law and the results are in Table 9. This table only reflects the regression done on the stripping curve and is the same regardless of ozone or trichloroethylene concentration.

In addition to the graphical presentation of the data an analysis of variance for a three-factor experiment was performed. The three factors for the experiment were ozone concentration, air/water flow ratios, and with or without ultraviolet light. The results of these analyses are shown in Tables 10 and 11.

#### Toluene

The next set of data was the toluene samples. Due to time restraints only one concentration was evaluated. The samples were analyzed using a gas chromatograph equipped with a flame ionization detector. The resulting concentrations are shown in Table 12. As noted with the trichloroethylene the initial concentration was not exactly 1 mg/l but an average of 1.24 mg/l.

The toluene analysis method was consistent with the

Table 7

Percent Removal by Total Process, Stripping, and Reaction  
Trichloroethylene, Average Initial Concentration 1.32 mg/l

Without Ultraviolet radiation

Ozone Conc. (mg/l)		<u>Air/Water Flow Ratio (G/L)</u>			
		1	5	10	20
1	Total	62.26	79.16	86.78	85.68
	Stripping	25.92	63.62	77.77	85.68
	Reaction	36.35	15.54	9.01	0
3	Total	67.56	84.28	87.75	94.65
	Stripping	25.92	63.62	77.77	87.49
	Reaction	41.64	20.65	9.98	7.16
5	Total	66.12	79.09	86.88	90.87
	Stripping	25.92	63.62	77.77	87.49
	Reaction	40.21	15.47	9.11	3.38

With Ultraviolet Radiation

1	Total	77.71	75.18	83.34	88.48
	Stripping	25.92	63.62	77.77	87.49
	Reaction	51.79	11.56	5.57	0.99
3	Total	77.73	85.82	84.92	90.91
	Stripping	25.92	63.62	77.77	87.49
	Reaction	51.81	22.20	7.16	3.42
5	Total	79.25	81.11	90.08	93.71
	Stripping	25.92	63.62	77.77	87.49
	Reaction	53.33	17.48	12.31	6.21



Table 8

Percent Removal by Total Process, Stripping, and Reaction  
Trichloroethylene, Average Initial Concentration 12.89 mg/l

Without Ultraviolet radiation

Ozone Conc. (mg/l)	<u>Air/Water Flow Ratio (G/L)</u>			
	1	5	10	20
1 Total	57.79	72.84	81.87	89.78
Stripping	25.92	63.62	77.77	85.68
Reaction	31.88	9.22	4.10	2.28
3 Total	63.54	76.26	86.10	90.32
Stripping	25.92	63.62	77.77	87.49
Reaction	37.63	12.64	8.34	2.83
5 Total	76.54	81.94	84.28	87.90
Stripping	25.92	63.62	77.77	87.49
Reaction	50.63	18.31	6.51	0.40

With Ultraviolet Radiation

1 Total	64.32	77.03	85.75	87.82
Stripping	25.92	63.62	77.77	87.49
Reaction	38.40	13.41	7.99	0.33
3 Total	62.53	68.77	83.26	89.85
Stripping	25.92	63.62	77.77	87.49
Reaction	36.61	5.15	5.49	2.36
5 Total	70.12	81.02	89.31	89.93
Stripping	25.92	63.62	77.77	87.49
Reaction	44.21	17.39	11.54	2.43

Figure 7  
TCE(1.32mg/l) Reacted With 1mg/l Ozone

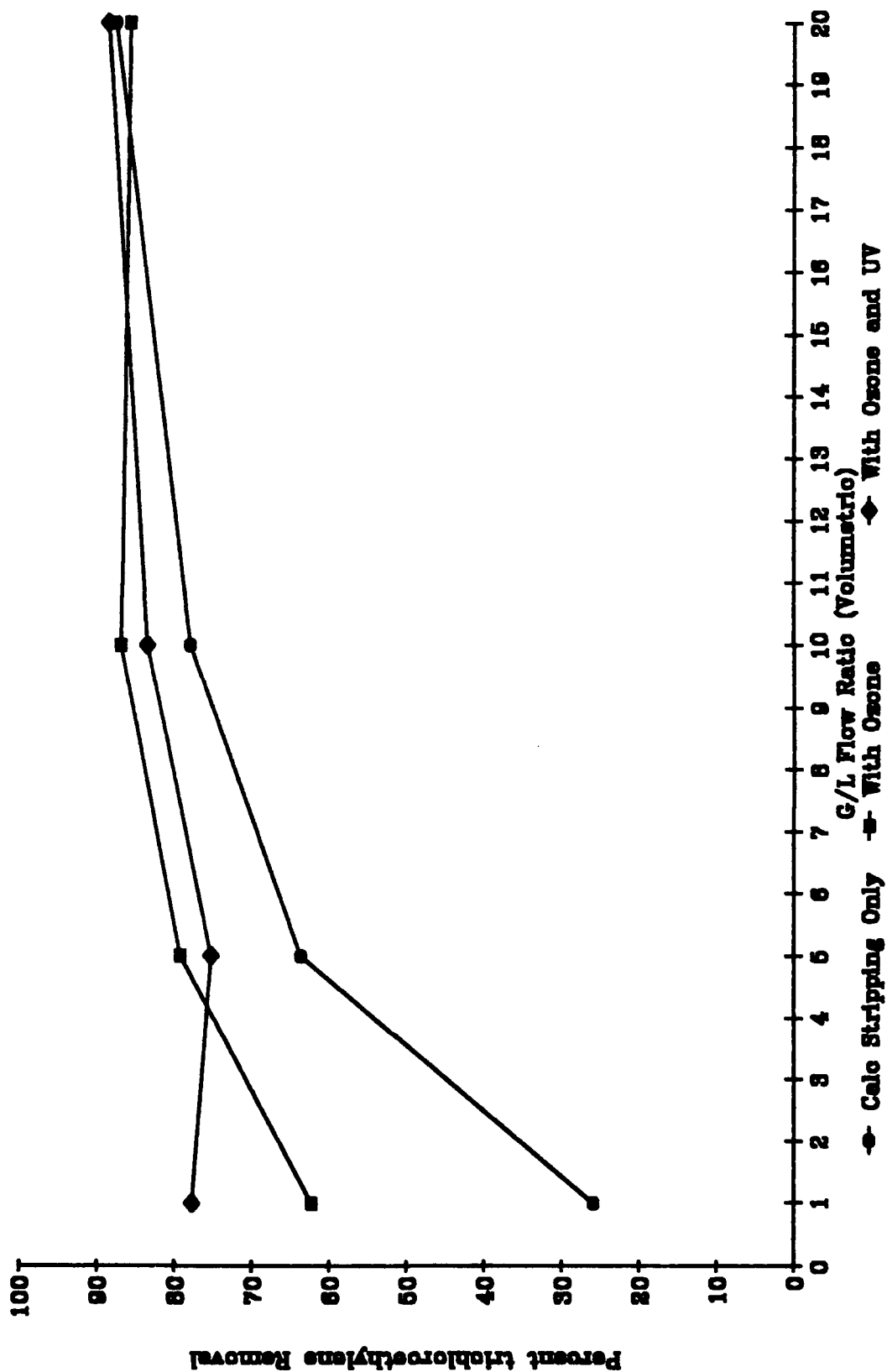


Figure 8  
TCE(1.32mg/l) Reacted With 3mg/l Ozone

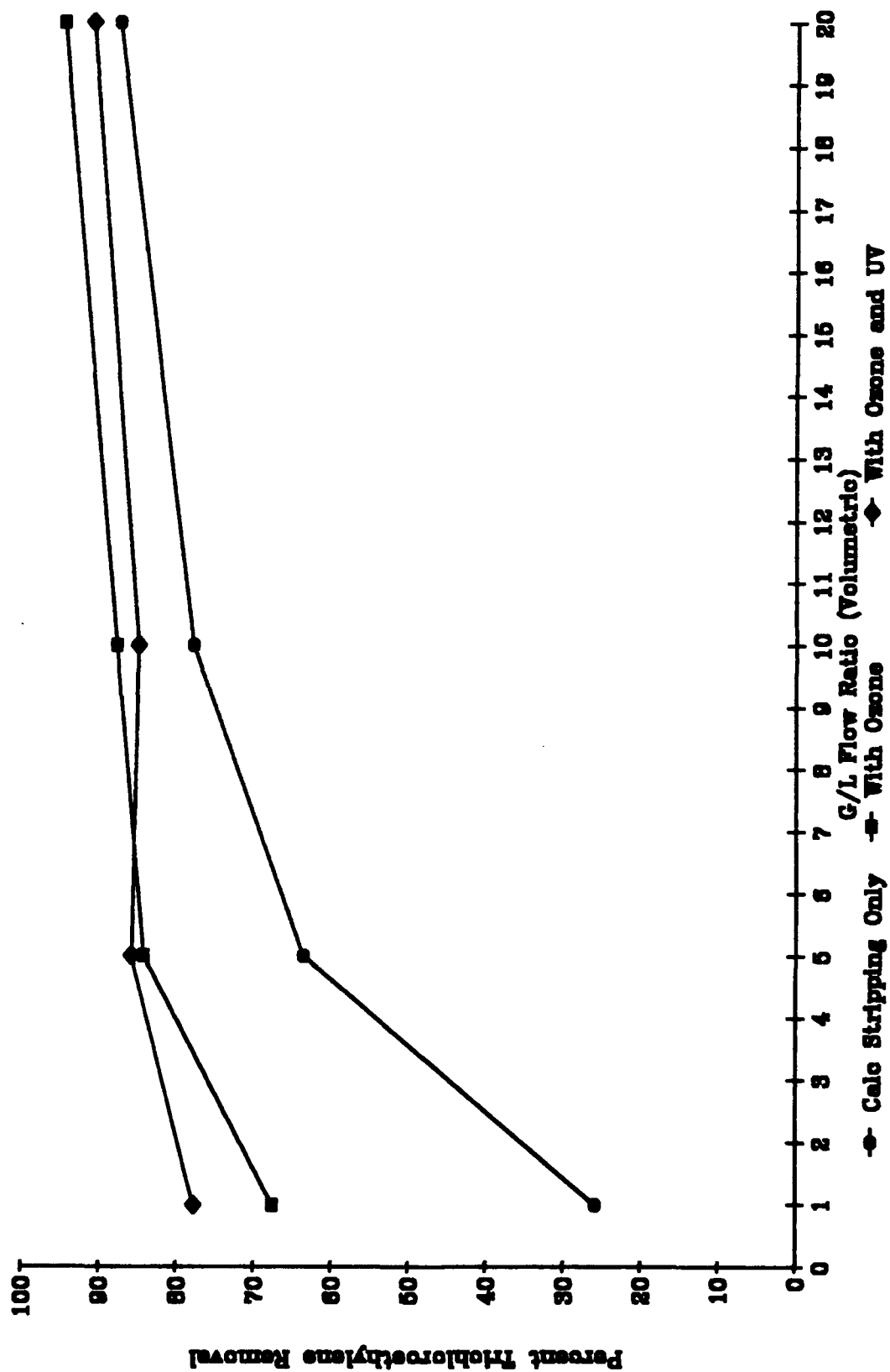


Figure 9  
TCE(1.32mg/l) Reacted With 6mg/l Ozone

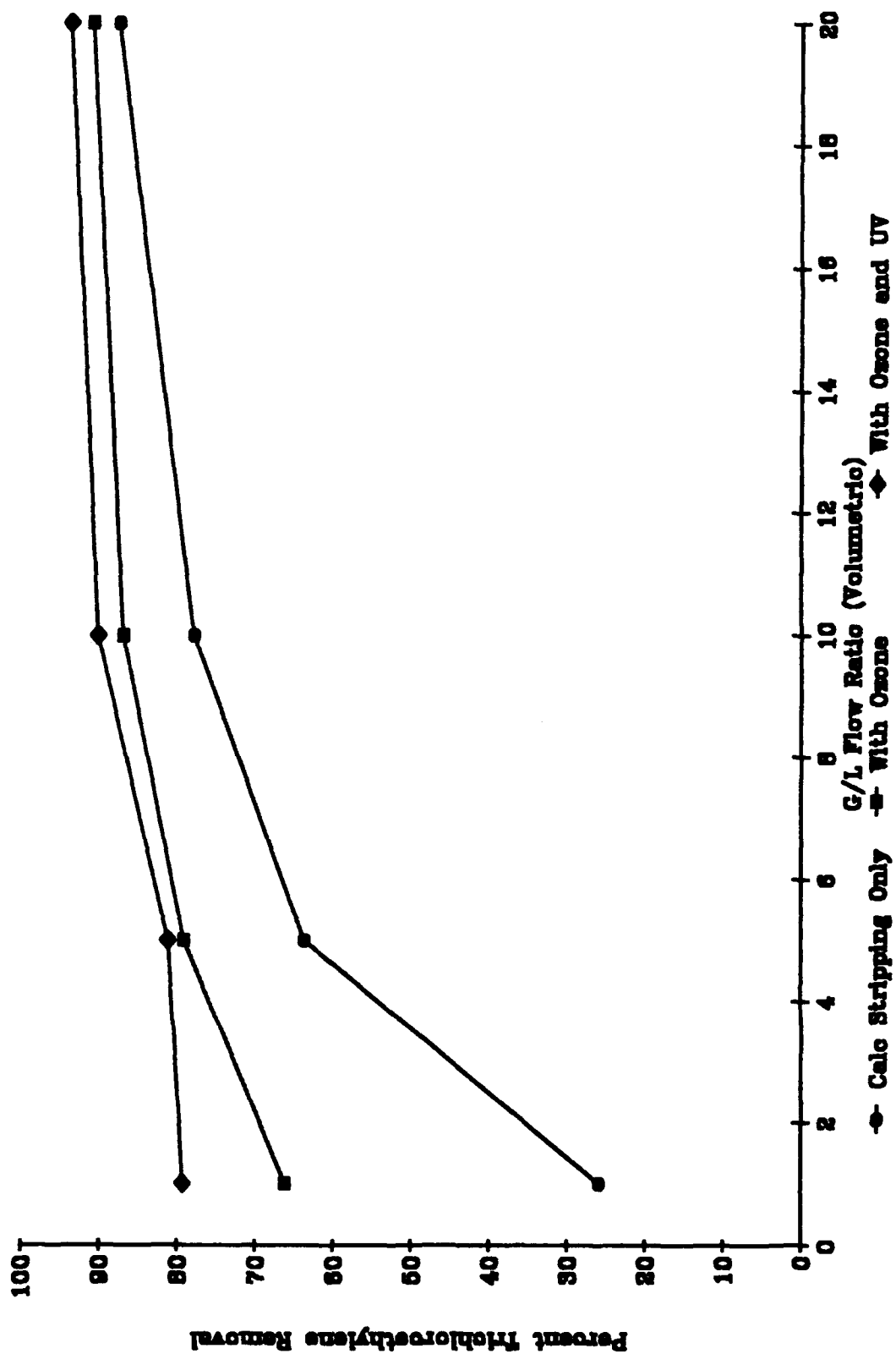


Figure 10  
TCE, 12.89mg/l Reacted With 1mg/l Ozone

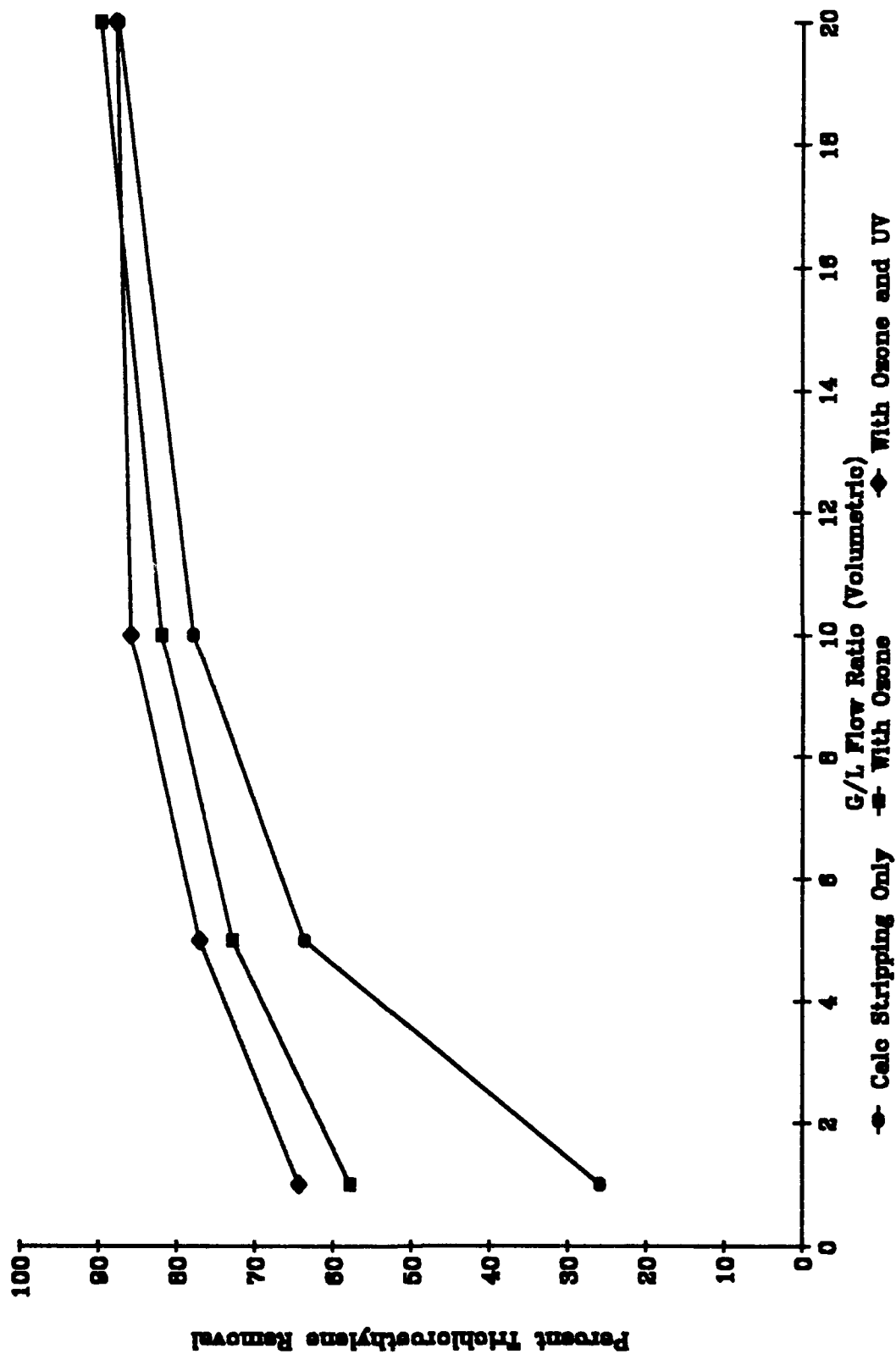


Figure 11  
TCE, 12.89mg/l Reacted With 3mg/l Ozone

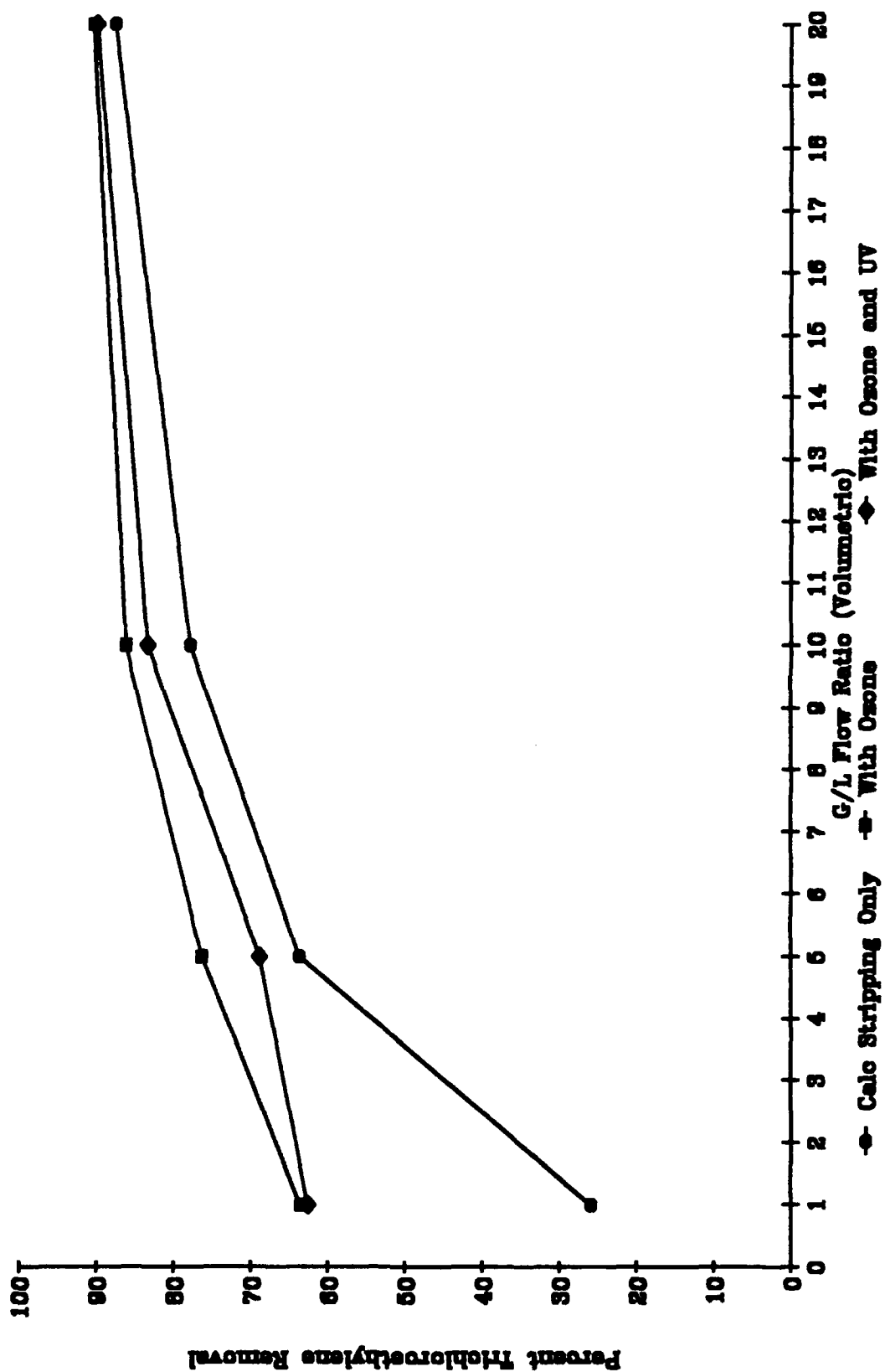


Figure 12  
TCE, 12.89mg/l Reacted With 5mg/l Ozone

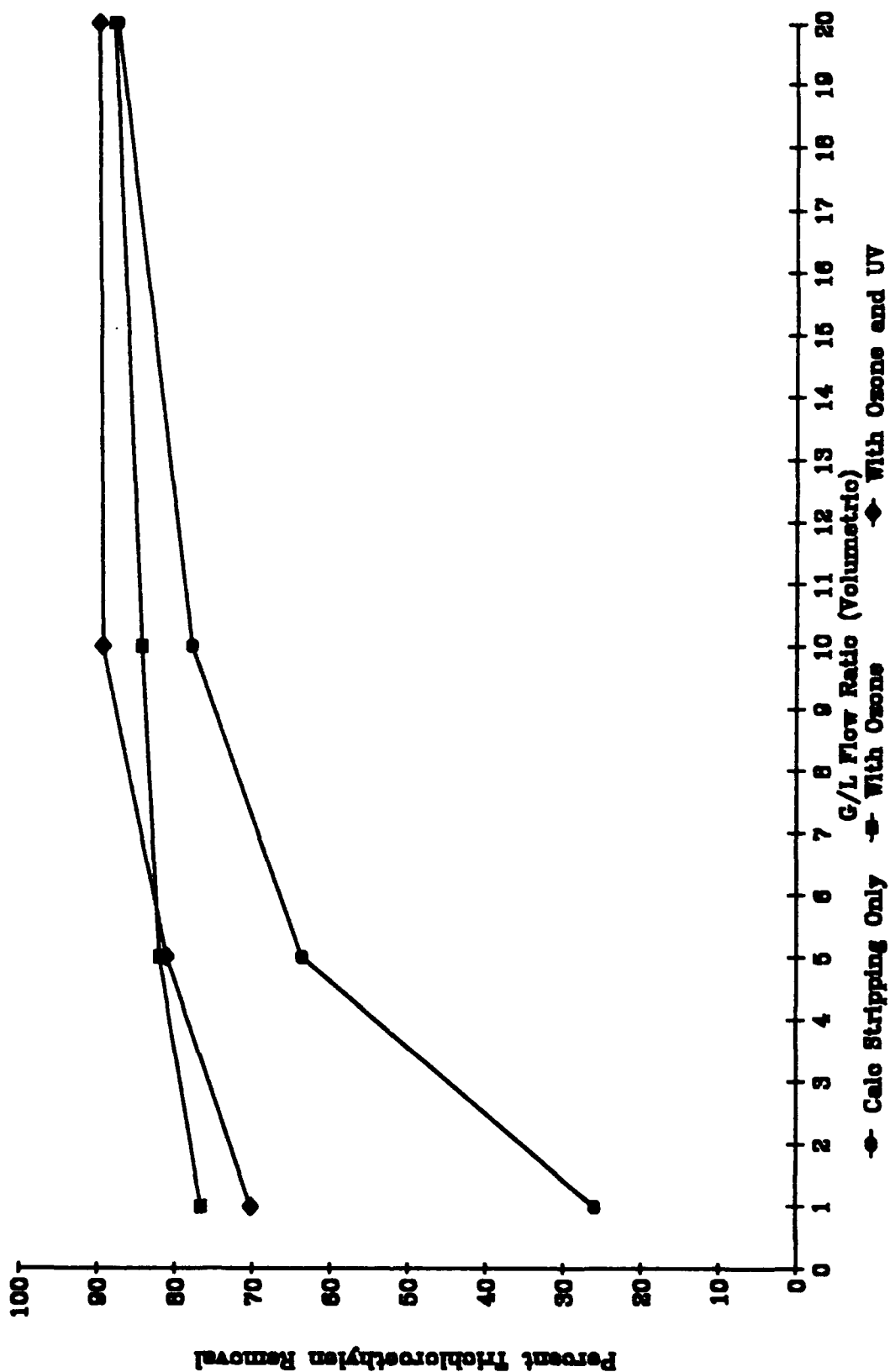


Table 9Simple Regression Results for Stripping Data for TCE

Comp F	Crit F*	Corr Coef	Coef of Det	Regression Equation
215.08	98.5	0.99	0.99	$y = 27.49 + 20.97 \ln X$

\* Critical F-statistic of 18.5 for 5% level of significance and 98.5 for 1% level of significance

' Ronald E. Walpole and Raymond H Meyers, Probability and Statistics for Engineers and Scientists, 4th ed. (New York: MacMillan, 1989), 701-707.



Table 10

Analysis of Variance for Three-Factor Experiment on Percent Removal of TCE, Average Initial Concentration 1.32 mg/l

<u>Source of Variation</u>	<u>Sum of Squares</u>	<u>Degrees of Freedom</u>	<u>Mean Square</u>	<u>Computed F</u>	<u>Critical F'</u>
<u>Main Effect</u>					
G/L	6400.99	3.0	2133.66	500.22	4.76
Ozone	77.41	2.0	38.70	9.07	5.14
UV	52.01	1.0	52.01	12.19	5.99
<u>Two-Factor Interaction</u>					
G/L & Ozone	35.30	6.0	5.88	1.38	4.28
G/L & UV	199.58	3.0	66.53	15.60	4.76
Ozone & UV	17.44	2.0	8.72	2.04	5.14
<u>Three-Factor Interaction</u>					
Error	25.59	6.0	4.27		
Total	6808.31	23.0			

<sup>1</sup> Ronald E. Walpole and Raymond H Meyers, Probability and Statistics for Engineers and Scientists, 4th ed. (New York: MacMillan, 1989), 701-707.

Table 11Analysis of Variance for Three-Factor Experiment on Percent Removal of TCE, Average Initial Concentration 12.89 mg/l

<u>Source of Variation</u>	<u>Sum of Squares</u>	<u>Degrees of Freedom</u>	<u>Mean Square</u>	<u>Computed F</u>	<u>Critical F'</u>
<u>Main Effect</u>					
G/L	5149.00	3.0	1716.33	168.23	4.76
Ozone	148.37	2.0	74.19	7.27	5.14
UV	0.01	1.0	0.01	0.00	5.99
<u>Two-Factor Interaction</u>					
G/L & Ozone	122.78	6.0	20.46	2.01	4.28
G/L & UV	9.26	3.0	3.09	0.30	4.76
Ozone & UV	37.49	2.0	18.75	1.84	5.14
<u>Three-Factor Interaction</u>					
Error	61.22	6.0	10.20		
Total	5528.14	23.0			

' Ronald E. Walpole and Raymond H Meyers, Probability and Statistics for Engineers and Scientists, 4th ed. (New York: MacMillan, 1989), 701-707.

Table 12  
Percent Removal of Toluene,  
Average Initial Concentration 1.24 mg/l

<u>G/L</u> <u>Ratio</u>	<u>Ozone</u> <u>(mg/l)</u>	<u>UV</u> <u>Light</u>	<u>Influent</u> <u>Conc(ug/l)</u>	<u>Effluent</u> <u>Conc(ug/l)</u>	<u>Percent</u> <u>Removal</u>
1	0	NO	958.35	319.68	66.64
5	0	NO	958.35	295.25	69.19
10	0	NO	958.35	155.31	83.79
20	0	NO	958.35	244.92	74.44
1	1	NO	958.35	716.39	25.25
5	1	NO	958.35	404.77	57.76
10	1	NO	958.35	269.50	71.88
20	1	NO	958.35	134.30	85.99
1	3	NO	958.35	351.50	63.32
5	3	NO	958.35	194.88	79.67
10	3	NO	958.35	138.45	85.55
20	3	NO	958.35	117.90	87.70
1	5	NO	958.35	259.82	72.89
5	5	NO	958.35	-	-
10	5	NO	958.35	-	-
20	5	NO	958.35	-	-
1	1	YES	1521.91	301.49	80.19
5	1	YES	1521.91	274.11	81.99
10	1	YES	1521.91	172.37	88.67
20	1	YES	1521.91	135.32	91.11
1	3	YES	1521.91	404.15	73.44
5	3	YES	1521.91	272.12	82.12
10	3	YES	1521.91	234.45	84.59
20	3	YES	1521.91	475.23	68.77
1	5	YES	1521.91	307.05	79.82
5	5	YES	1521.91	278.69	81.69
10	5	YES	1521.91	172.17	88.69
20	5	YES	1521.91	165.47	89.13

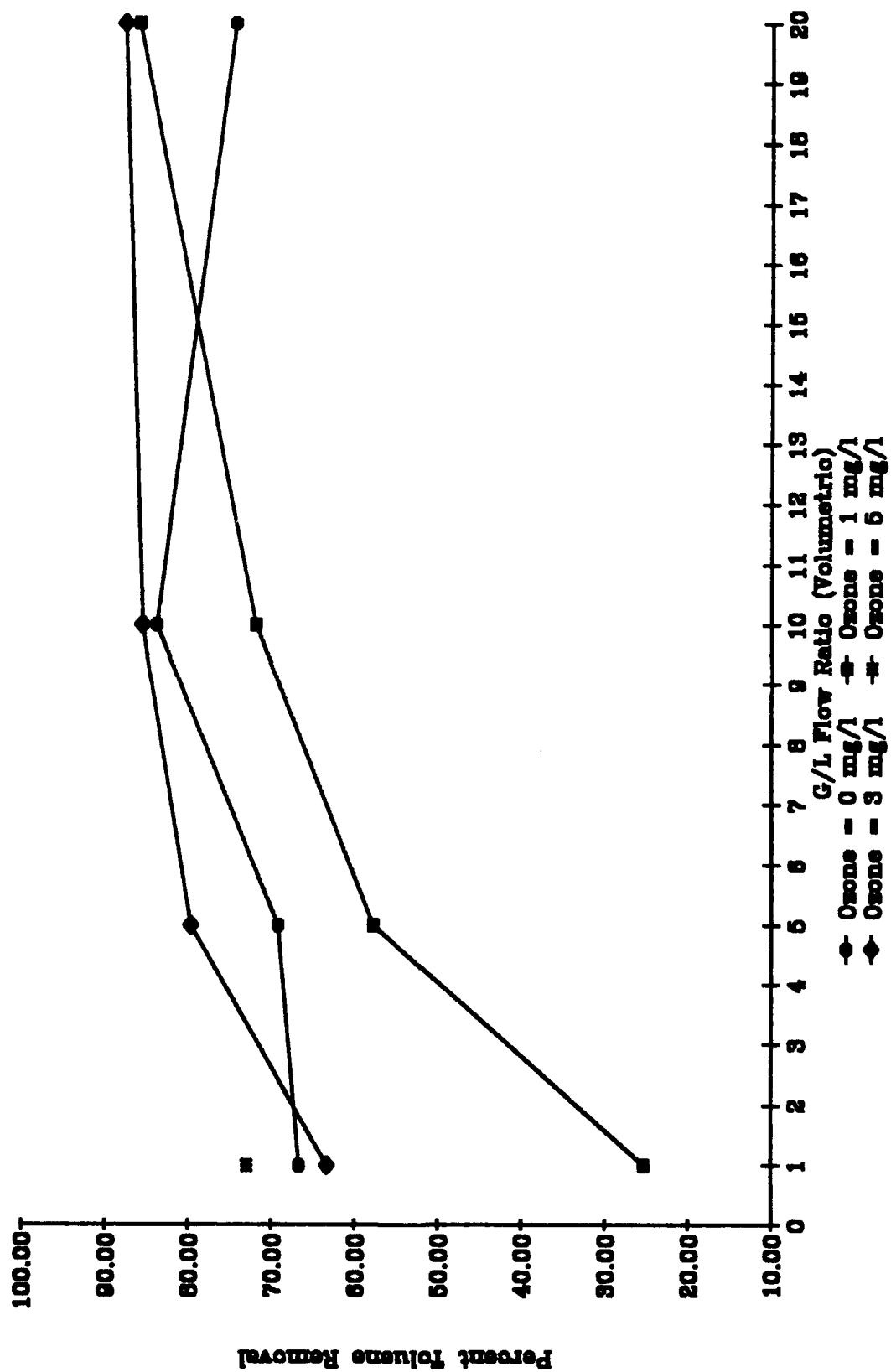
trichloroethylene analysis. First the data was plotted and a graph was drawn of volumetric air/water flow ratio vs. percent removal for the different ozone concentrations. These graphs are shown in Figures 13 and 14.

The same assumptions concerning stripping vs. reaction were made for the toluene as were the trichloroethylene. The same equation using Henry's Law constant and procedures, used for the trichloroethylene, were used to determine the amount of toluene stripped and reacted. This data is presented in tabular form in Table 13 and graphically in Figures 15, 16, and 17. Again a simple regression was performed on each set of data and the results are tabulated in Table 14. Multiple regressions were also accomplished and those results are in Table 15. As with the trichloroethylene an analysis of variance for a three-factor experiment was performed with the results tabulated in Table 16.

#### Salicylic Acid

The salicylic acid samples were the last to be analyzed and the tabulated results are shown in Tables 17 and 18 and a graphical representation of those results are shown in Figures 18, 19, 20 and 21. Again, the initial concentrations of nonpurgable organic carbon were not exactly 1 and 10 mg/l. As seen in Figures 18 and 19 the data was plotted in the same format as the trichloroethylene and toluene tests. The analysis of the

Figure 13  
Toluene Removal, Initial Conc 1.24 mg/l



**Figure 14**  
**Toluene Removal, Initial Conc 1.24 mg/l**

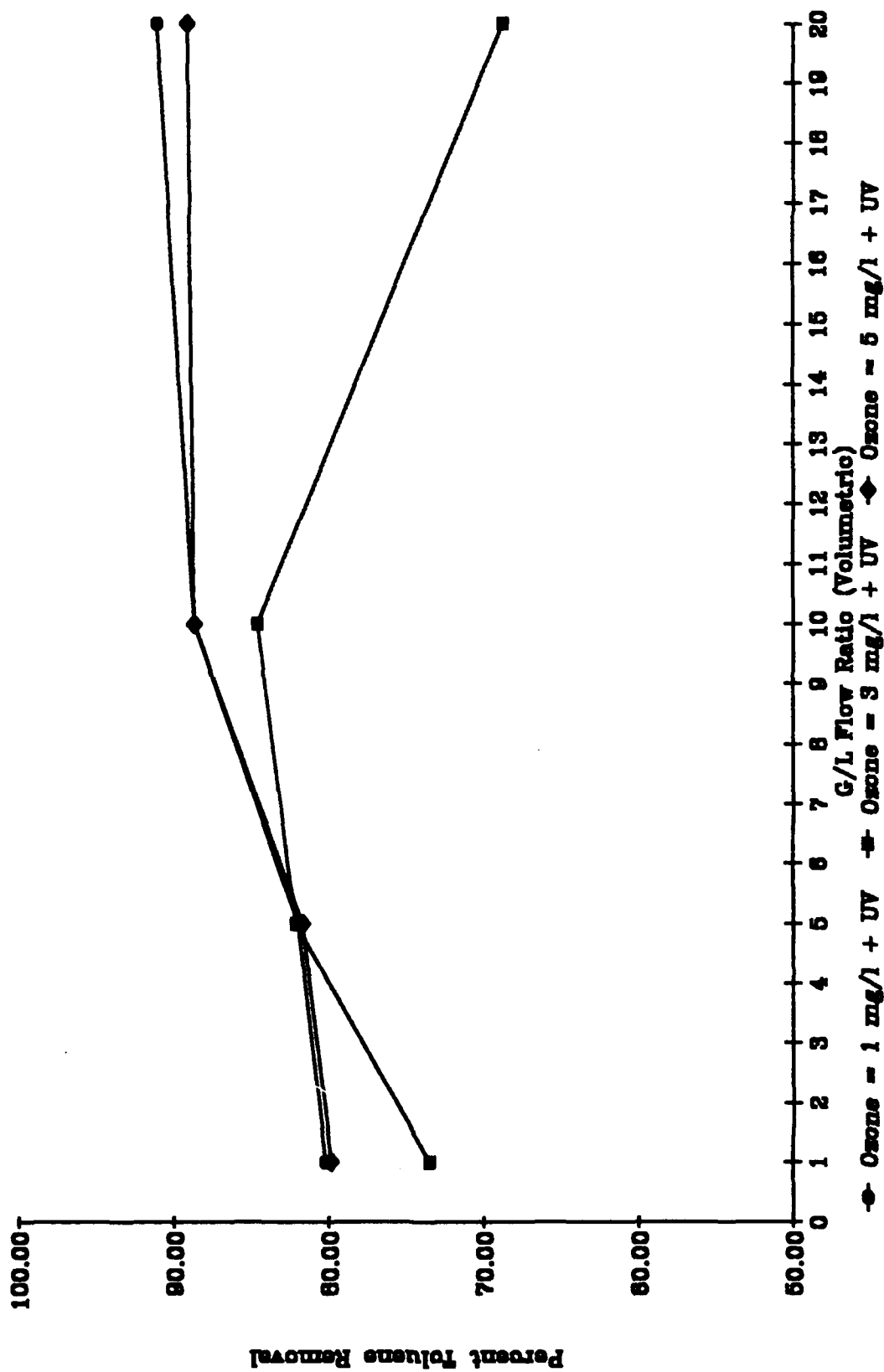


Table 13

Percent Removal by Total Process, Stripping, and Reaction  
For Toluene, Average Initial Concentration 12.89 mg/l

Without Ultraviolet Radiation

Ozone Conc. (mg/l)	<u>Air/Water Flow Ratio (G/L)</u>			
	1	5	10	20
1 Total	25.25	57.76	71.88	85.99
Stripping	20.78	56.74	72.40	83.99
Reaction	4.47	1.02	0	2.00
3 Total	63.32	79.67	85.55	87.70
Stripping	20.78	56.74	72.40	83.99
Reaction	42.54	22.93	13.15	3.71
5 Total	72.89	-	-	-
Stripping	20.78	56.74	72.40	83.99
Reaction	52.11	-	-	-

With Ultraviolet Radiation

1 Total	80.19	81.99	88.67	91.11
Stripping	20.78	56.74	72.40	83.99
Reaction	59.41	25.25	16.27	7.12
3 Total	73.44	82.12	84.59	68.77
Stripping	20.78	56.74	72.40	83.99
Reaction	52.66	25.38	12.19	0
5 Total	79.82	81.69	88.69	89.13
Stripping	20.78	56.74	72.40	83.99
Reaction	59.04	24.95	16.29	5.14

Figure 15  
Tol. 1.24mg/l Reacted with 1mg/l Ozone

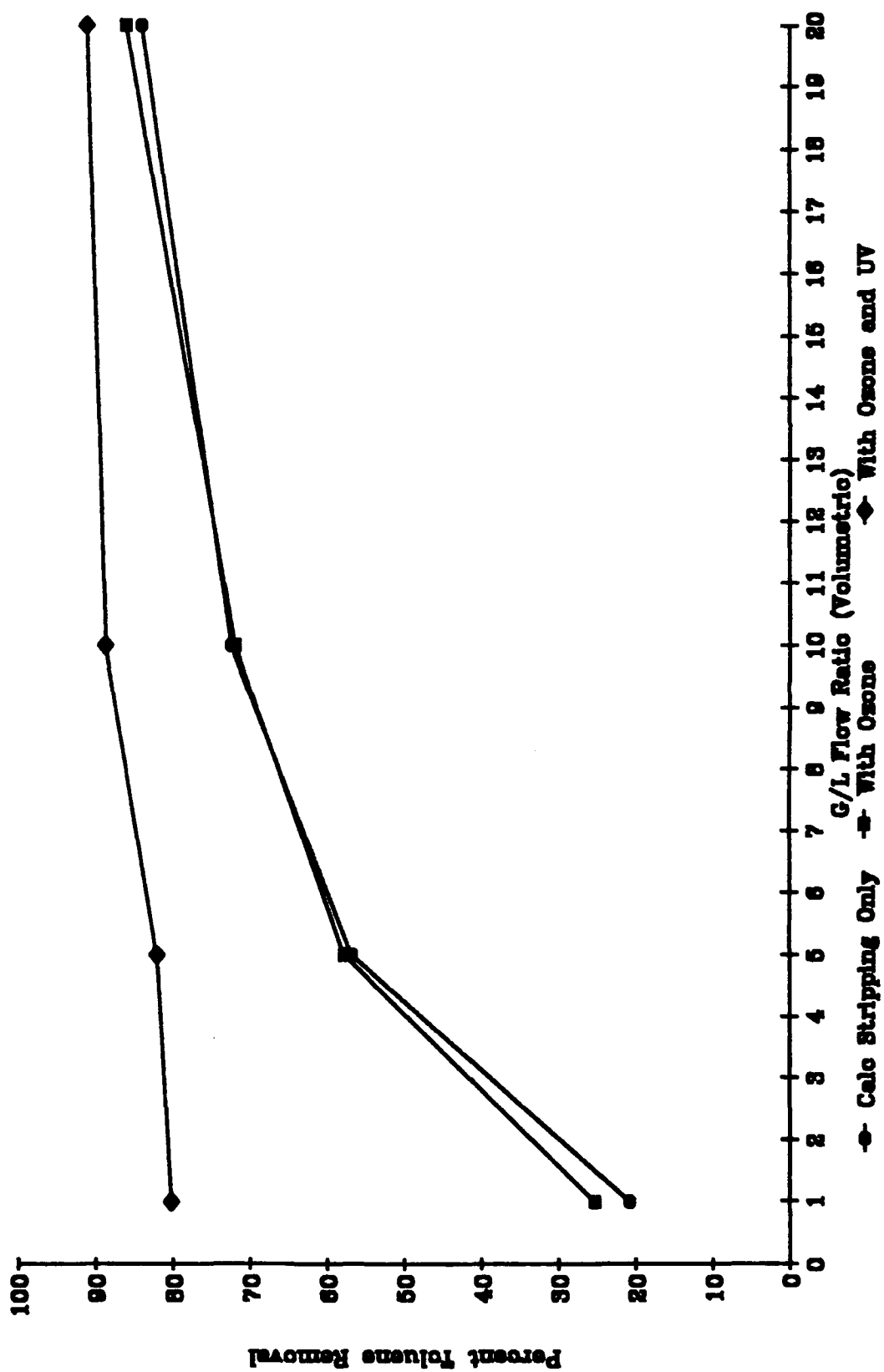




Figure 16  
Tot. 1.24mg/l Reacted With 3mg/l Ozone

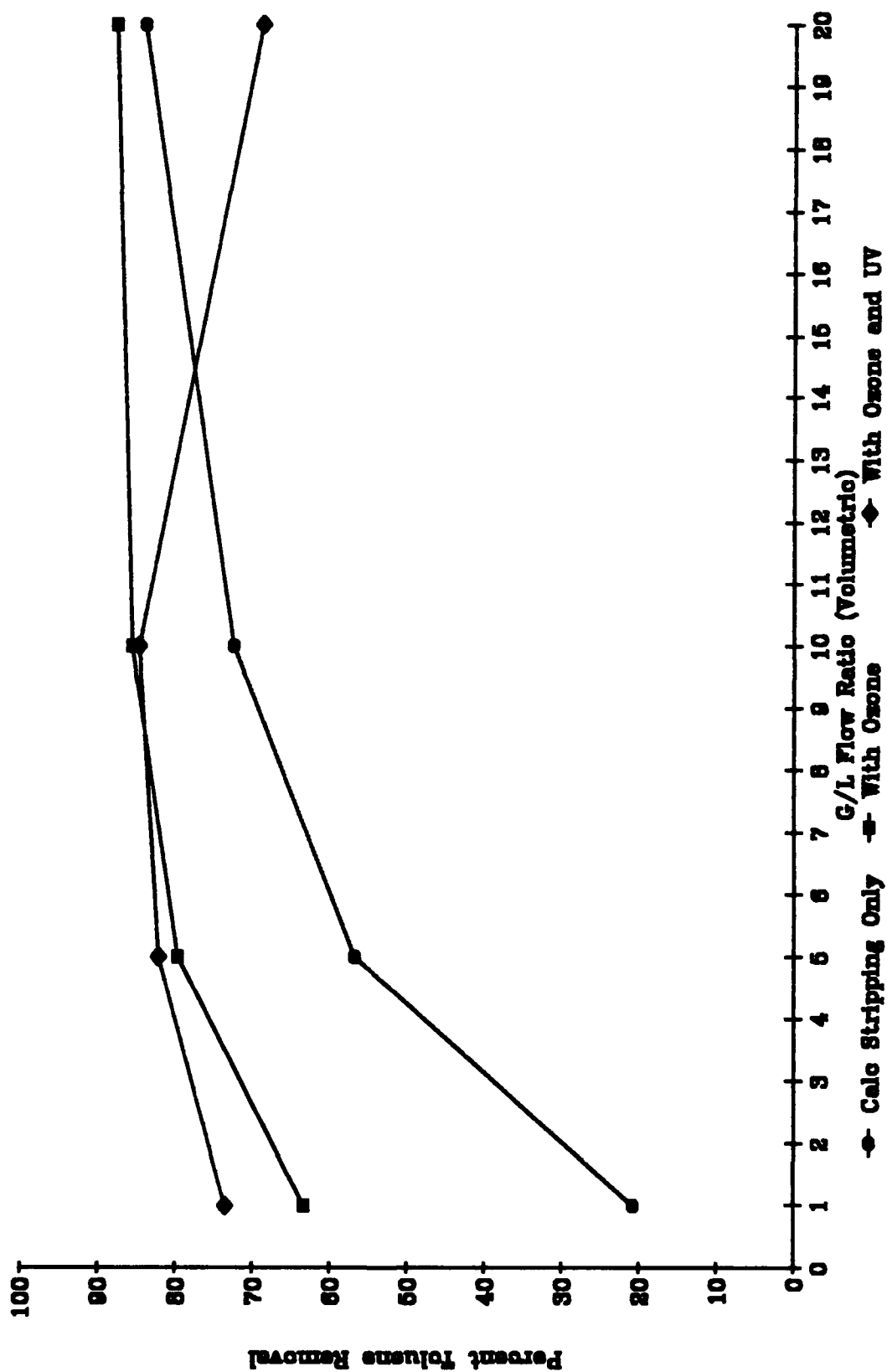


Figure 17  
Tol. 1.24mg/l Reacted With 5mg/l Ozone

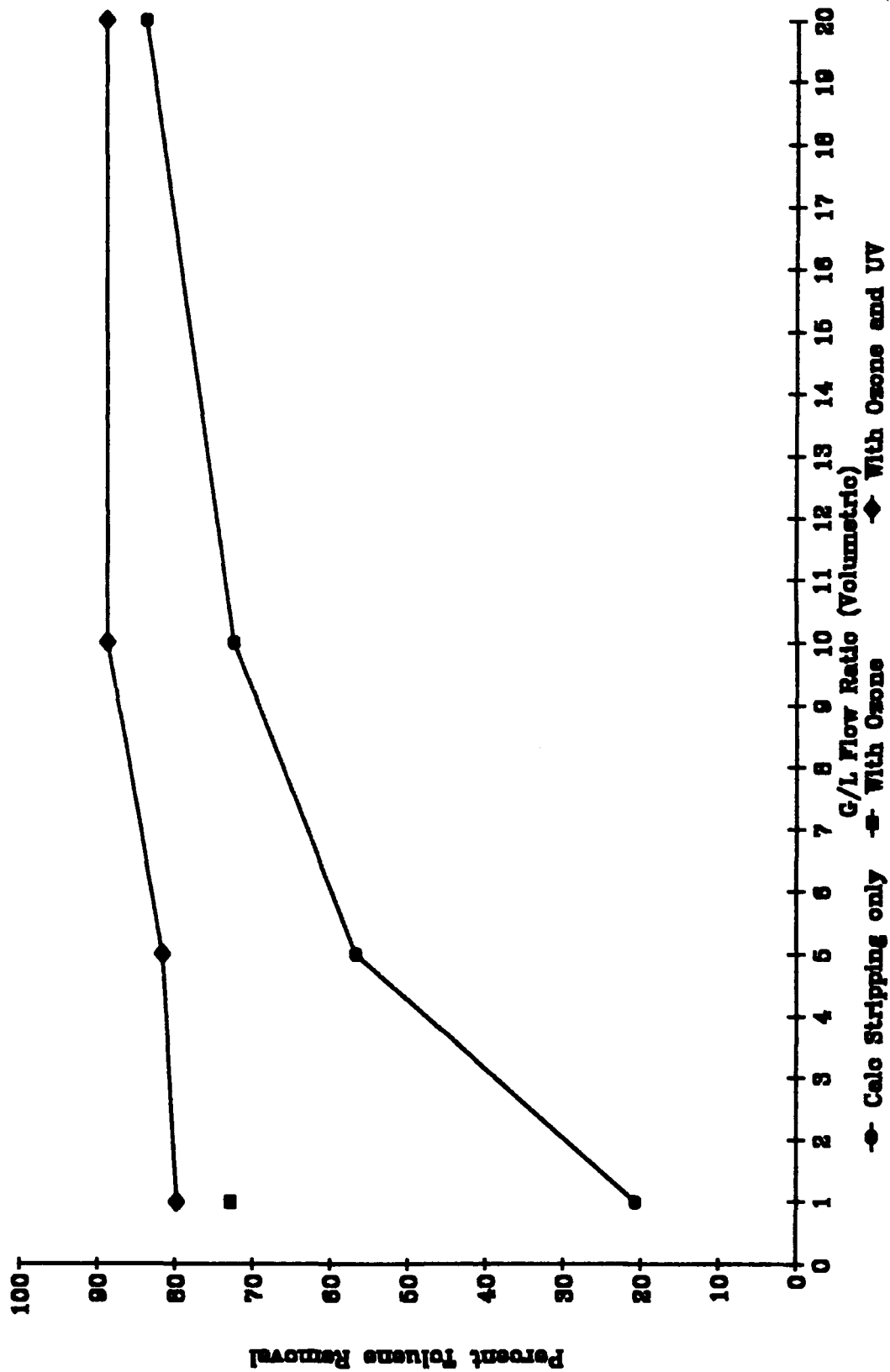


Table 14  
Simple Regression Results for Toluene With  
Initial Average Concentration of 1.24 mg/l

Without UV

Ozone mg/l	Comp F	Crit F*	Corr Coef	Coef of Det	Regression Equation
1	5X10 <sup>5</sup>	98.5	1.00	1.00	$y = 25.22 + 20.27 \ln X$
3	353.99	98.5	0.98	0.97	$y = 64.44 + 8.47 \ln X$
5	Only one data point.				

With UV

Ozone mg/l	Comp F	Crit F	Corr Coef	Coef of Det	Regression Equation
1	16.08	18.5	0.94	0.89	$y = 80.08 + 0.60X$
3	0.41	18.5	-0.41	0.17	$y = 80.57 - 0.37X$
5	9.52	18.5	0.91	0.83	$y = 78.99 + 3.38 \ln X$

Simple Regression Results for Stripping for Toluene

Comp F	Crit F	Corr Coef	Coef of Det	Regression Equation
697.53	98.5	0.99	0.99	$y = 21.52 + 21.41 \ln X$

\* Critical F-statistic of 18.5 for 5% level of significance and 98.5 for 1% level of significance

' Ronald E. Walpole and Raymond H Meyers, Probability and Statistics for Engineers and Scientists, 4th ed. (New York: MacMillan, 1989), 701-707.

Table 15

**Multiple Regression Results for Toluene With  
Initial Average Concentration of 1.24 mg/l**

y = percent removal  
X1 = G/L ratio  
X2 = ozone concentration, mg/l

Without UV

Regression Equation	:	$y = 34.43 + 2.08X_1 + 8.02X_2$
Computed F-statistic	:	8.61
Critical F-statistic*	:	8.02
Computed t-statistic	:	
b1	:	4.58
b2	:	3.29
Critical t-statistic <sup>1</sup>	:	
t <sub>0.01</sub>	:	3.14
t <sub>0.05</sub>	:	3.14
Correlation Coeff.	:	0.86
Coeff. of Determination	:	0.74

With UV

Regression Equation	:	$y = 80.78 + 0.25X_1 - 0.16X_2$
Computed F-statistic	:	0.38
Critical F-statistic	:	8.02
Computed t-statistic	:	
b1	:	1.01
b2	:	0.15
Critical t-statistic	:	
t <sub>0.01</sub>	:	0.88
t <sub>0.05</sub>	:	0.13
Correlation Coeff.	:	0.92
Coeff. of Determination	:	0.85

\* Critical F-statistic of 18.5 for 5% level of significance and 98.5 for 1% level of significance

<sup>1</sup> Ronald E. Walpole and Raymond H Meyers, Probability and Statistics for Engineers and Scientists, 4th ed. (New York: MacMillan, 1989), 701-707.

Table 16

Analysis of Variance for Three-Factor Experiment Percent  
Removal of Toluene, Avg. Initial Concentration 1.24 mg/l

<u>Source of Variation</u>	<u>Sum of Squares</u>	<u>Degrees of Freedom</u>	<u>Mean Square</u>	<u>Computed F</u>	<u>Critical F</u>
<u>Main Effect</u>					
G/L	1731.01	3.0	577.00	7.42	4.76
Ozone	2242.89	2.0	1121.45	14.43	5.14
UV	637.36	1.0	637.36	8.20	5.99
<u>Two-Factor Interaction</u>					
G/L & Ozone	950.64	6.0	158.44	2.04	4.28
G/L & UV	271.90	3.0	90.63	1.17	4.76
Ozone & UV	693.49	2.0	346.75	4.46	5.14
<u>Three-Factor Interaction</u>					
Error	466.37	6.0	77.73		
Total	6993.67	23.0			

' Ronald E. Walpole and Raymond H Meyers, Probability and Statistics for Engineers and Scientists, 4th ed. (New York: MacMillan, 1989), 701-707.

Table 17

Percent Removal of Nonpurgable Organic Carbon for  
Salicylic Acid, Average Initial Concentration 1.72 mg/l

<u>G/L Ratio</u>	<u>Ozone (mg/l)</u>	<u>UV Light</u>	<u>Influent Conc(mg/l)</u>	<u>Effluent Conc(mg/l)</u>	<u>Percent Removal</u>
1	0	NO	1.86	1.92	0
5	0	NO	1.86	1.80	3.01
10	0	NO	1.86	1.71	8.33
20	0	NO	1.86	1.58	15.05
1	1	NO	1.86	1.68	9.62
5	1	NO	1.86	1.54	17.04
10	1	NO	1.86	1.55	16.72
20	1	NO	1.86	1.43	22.90
1	3	NO	1.86	1.51	19.03
5	3	NO	1.86	1.59	14.41
10	3	NO	1.86	1.27	31.83
20	3	NO	1.86	1.23	33.87
1	5	NO	1.86	1.15	38.06
5	5	NO	1.86	1.23	33.92
10	5	NO	1.86	1.15	38.28
20	5	NO	1.86	1.05	43.76
1	1	YES	1.58	1.80	0
5	1	YES	1.58	1.79	0
10	1	YES	1.58	1.58	0
20	1	YES	1.58	1.69	0
1	3	YES	1.58	1.73	0
5	3	YES	1.58	1.48	6.32
10	3	YES	1.58	1.52	3.73
20	3	YES	1.58	1.36	13.84
1	5	YES	1.58	1.51	4.49
5	5	YES	1.58	1.39	12.14
10	5	YES	1.58	1.48	6.32
20	5	YES	1.58	1.64	0

Table 18

Percent Removal of Nonpurgable Organic Carbon for  
Salicylic Acid, Average Initial Concentration 10.47 mg/l

<u>G/L Ratio</u>	<u>Ozone (mg/l)</u>	<u>UV Light</u>	<u>Influent Conc(mg/l)</u>	<u>Effluent Conc(mg/l)</u>	<u>Percent Removal</u>
1	0	NO	10.33	10.26	0.68
5	0	NO	10.33	10.41	0
10	0	NO	10.33	10.87	0
20	0	NO	10.33	10.56	0
1	1	NO	10.33	10.60	0
5	1	NO	10.33	10.15	1.74
10	1	NO	10.33	10.14	1.84
20	1	NO	10.33	10.25	0.77
1	3	NO	10.33	10.19	1.36
5	3	NO	10.33	9.59	7.20
10	3	NO	10.33	9.47	8.36
20	3	NO	10.33	9.59	7.18
1	5	NO	10.33	9.99	3.32
5	5	NO	10.33	8.97	13.20
10	5	NO	10.33	9.41	8.94
20	5	NO	10.33	9.10	11.95
1	1	YES	10.61	10.82	0
5	1	YES	10.61	10.46	1.41
10	1	YES	10.61	10.41	1.89
20	1	YES	10.61	10.54	0.66
1	3	YES	10.61	10.61	0
5	3	YES	10.61	10.05	5.28
10	3	YES	10.61	10.05	5.28
20	3	YES	10.61	9.89	6.76
1	5	YES	10.61	10.09	4.90
5	5	YES	10.61	10.15	4.34
10	5	YES	10.61	9.53	10.20
20	5	YES	10.61	9.28	12.49

Figure 18  
Salicylic Acid, Initial Conc 1.72 mg/l

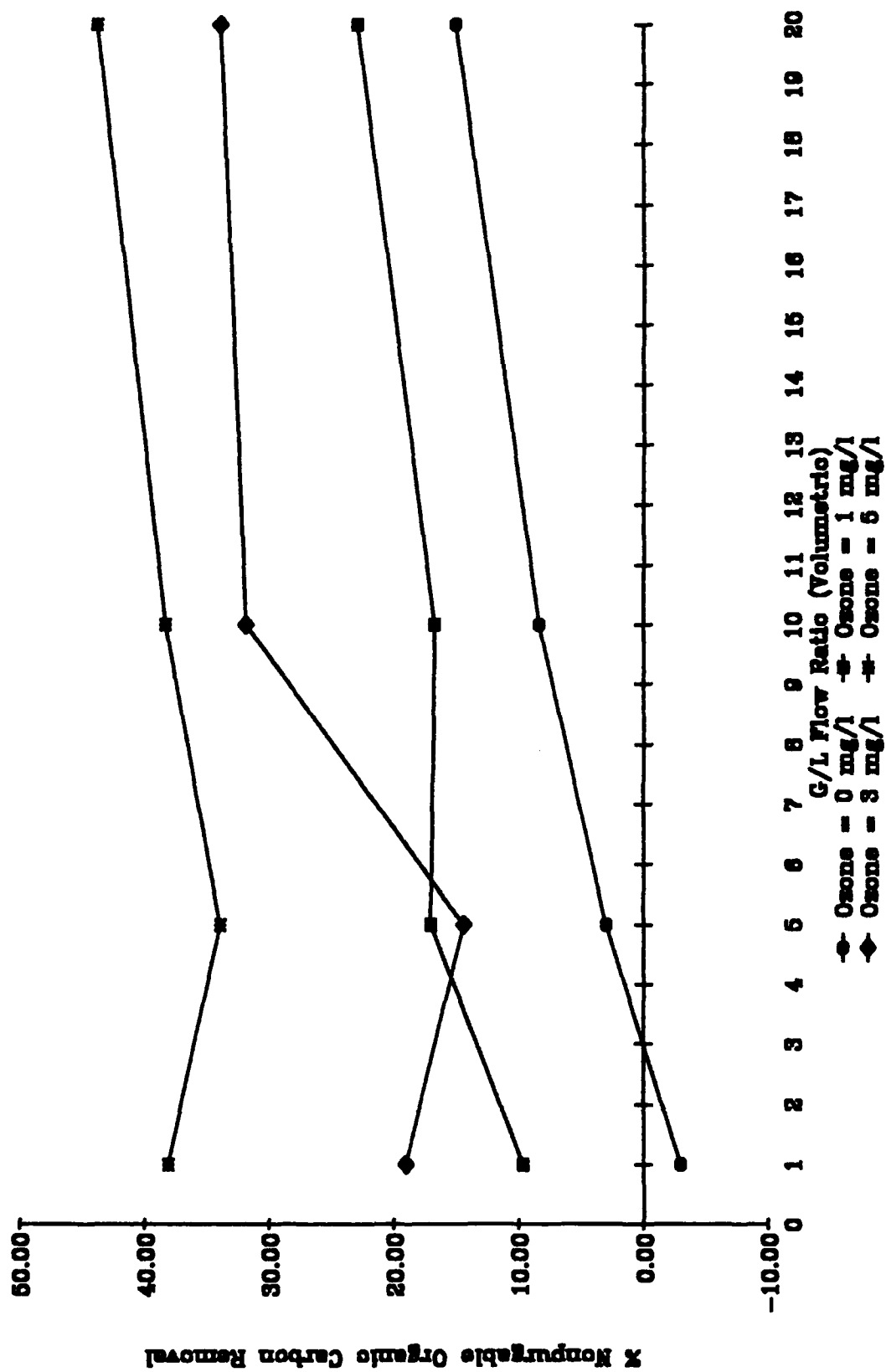




Figure 19  
Sulicylic Acid, Initial Conc 1.72 mg/l

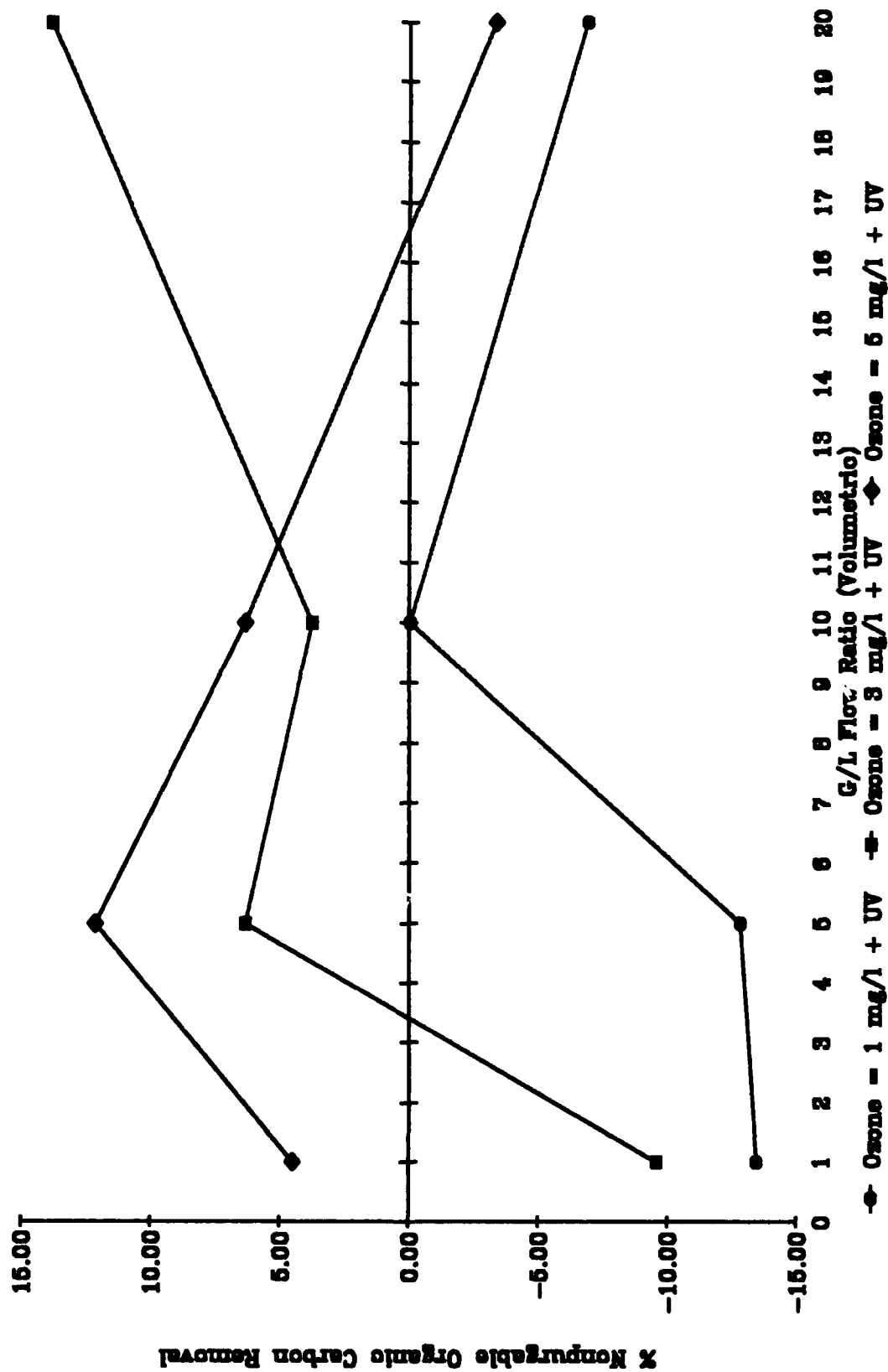


Figure 20  
Salicylic Acid Initial Conc 10.47 mg/l

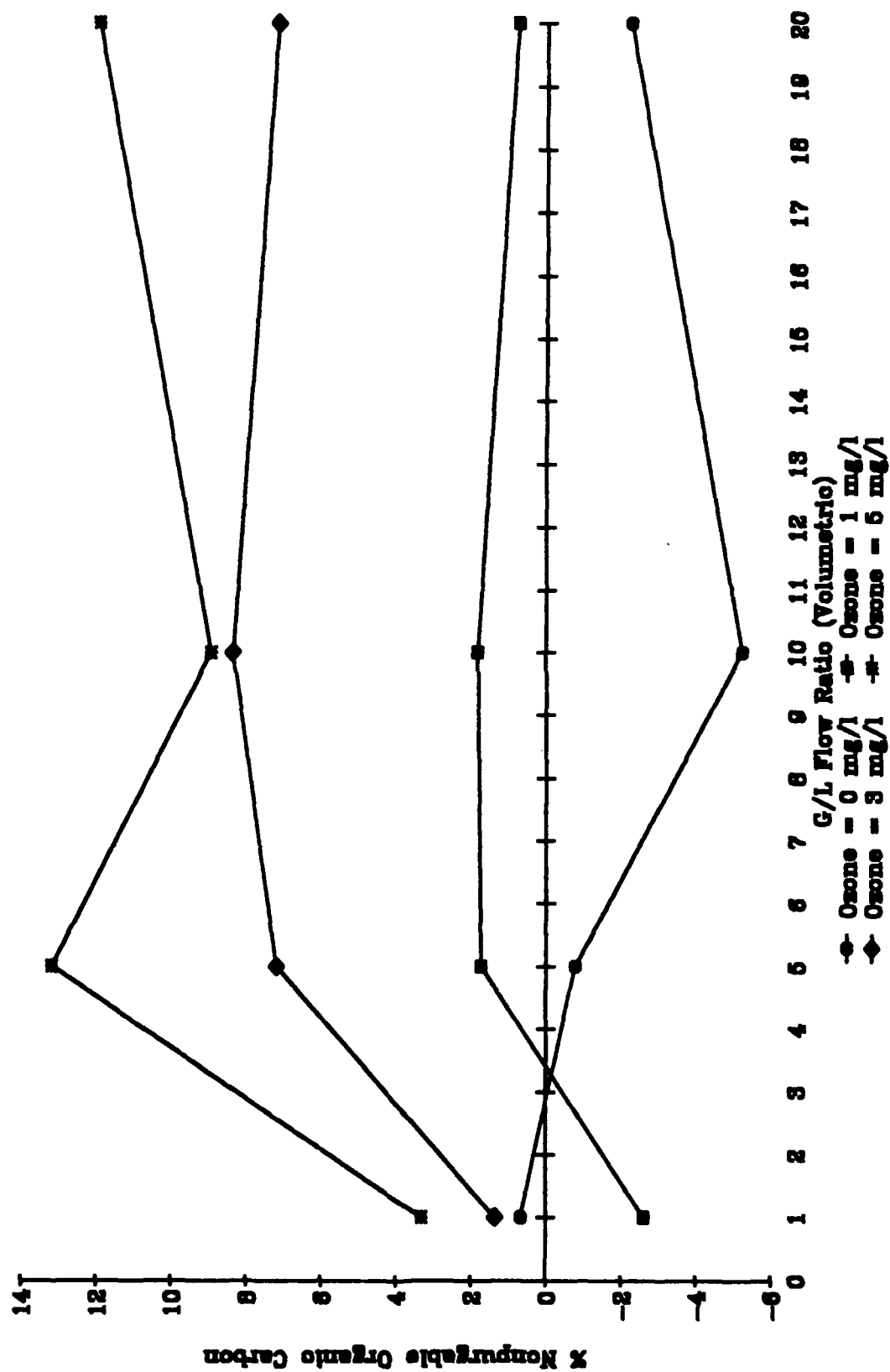
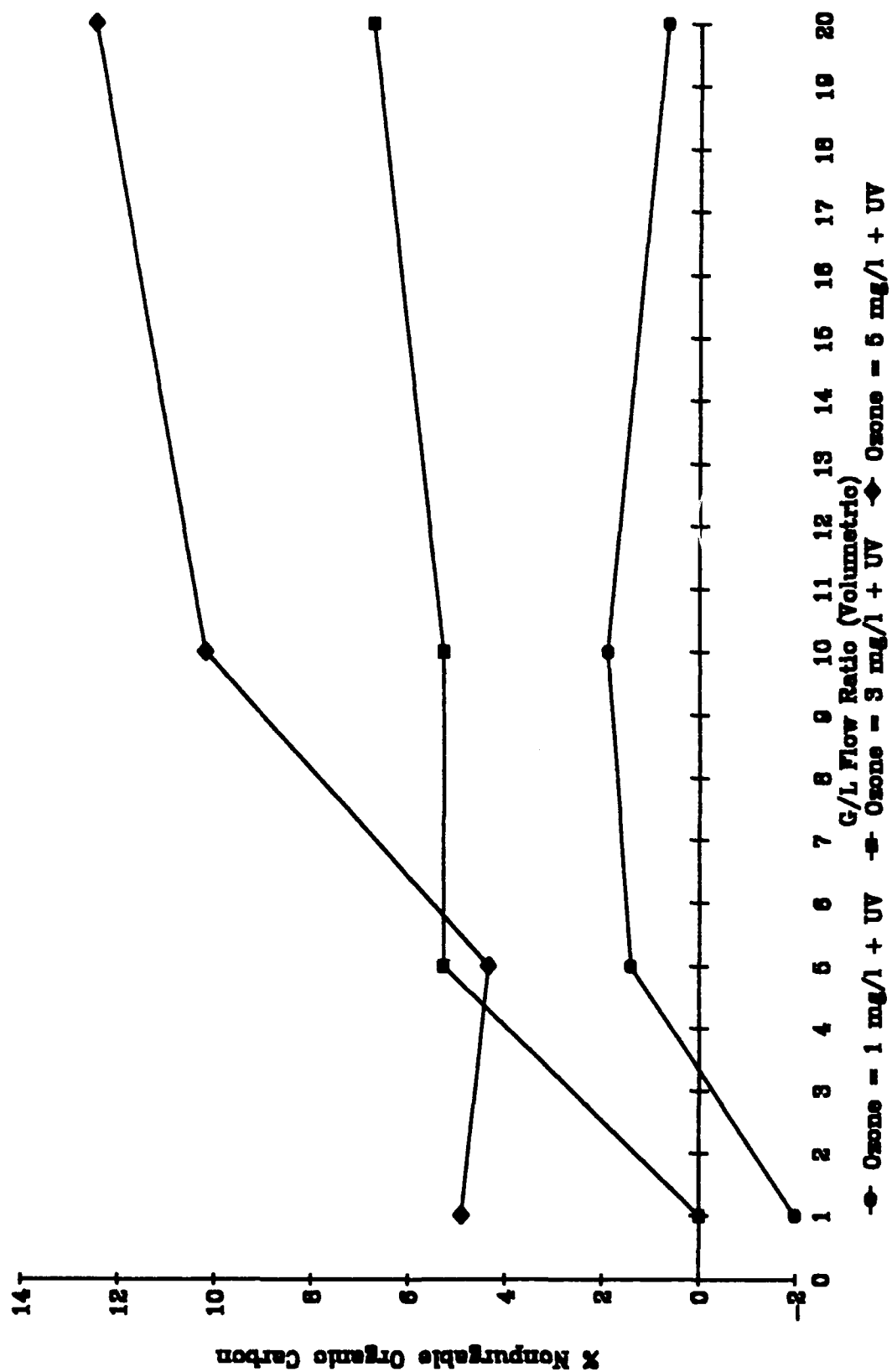


Figure 21  
Sulfoloic Acid, Initial Conc 10.47 mg/l



data provided some strange results. In several instances the amount of nonpurgable organic carbon actually increased. Because the reasons for the increase in nonpurgable organic carbon are unknown no further analyses of the salicylic acid data were performed.

## CHAPTER 5

### Evaluation and Interpretation of Results

The results of the experiment are promising. The evaluation and interpretation will be done in the same order as the data analysis, starting with trichloroethylene.

#### Trichloroethylene

The plotting of the data for the first trichloroethylene experiment indicates increased removal with the increase of any of the experimental factors; G/L ratios, ozone concentration, and use of ultraviolet light. The simple regression performed, using the F-statistic, indicated that most of the equations are statistically significant. The data from the tests without ultraviolet light were all transformed with a natural log function and the data with ultraviolet light were more linear. However, the latter set of data did not result in any statistically significant equations.

The second experimental test was with a higher concentration of trichloroethylene and also indicated, by observation of the plotted data, that removal was increased with an increase in experimental inputs. The higher concentration results also indicated that at lower G/L flow ratios the major contributing factor was the reaction between the ozone and/or ultraviolet and the contaminant. And, at higher G/L ratios the stripping of the contaminant

seemed to be the controlling removal factor.

The results from the multiple regression analyses on the trichloroethylene concentrations separately also indicate a high level of statistical significance, all above 1% level of significance using the F-statistic for the overall regression. With more data points to include in the analysis, all of the equations would prove statistically significant. The testing of the individual coefficients using the t-statistic resulted in most coefficients proving to be statistically significant above the 5% level of significance. The results from the combined data regression also proved to be statistically significant, on the same order as the individual data sets. However, the coefficient for the trichloroethylene concentration turned out to be negative. This means that as the concentration is increased the percent removal is decreased. This could be a result of overloading the column. The column diameter and volume of packing are limiting factors for stripping of compounds.

In order to determine if there is a significant effect due to any or all of the three experimental factors, an analysis of variance for three-factor experiments was performed on the data from the stripping and reaction calculations. This statistical analysis utilizes the F-test to evaluate the significance of a factor's contribution to the process of contaminant removal. The F-

statistic was evaluated at the 5% level of significance. The results indicate that the G/L flow ratio, ozone and ultraviolet light were all significant. However, the only interaction that proved significant was the interaction between the G/L ratio and the ultraviolet light at the lower trichloroethylene concentration.

Since the chloride samples did not work out, the assumption of equilibrium condition was made. When this data is plotted there are some apparent trends. It appears for both concentrations of trichloroethylene that at lower G/L flow ratios, removal is dominated by the reaction between the contaminant and ozone and/or ultraviolet light. As the G/L ratios are increased the process is dominated by stripping effects. This is due primarily to the large volume of air being applied not allowing enough time for the reaction between the contaminant with ozone and/or ultraviolet light to take place. The plots also indicate that there is an enhancement in contaminant percent removal from the addition of ultraviolet light to the system.

#### Toluene

The toluene experienced similar results to the trichloroethylene. Initial indications were that increasing any input factors increased the removal efficiency. The simple regression analysis of the data resulted in equations for the tests without the ultraviolet light showing levels of statistical significance above the

5% level of significance. The data from the tests with ultraviolet light showed a fairly high level of significance at the lower ozone concentration however, the level of significance decreased when the concentration of ozone was increased. After accomplishing the stripping and reaction calculations and then plotting the data, it appears that the addition of ultraviolet radiation has a significant affect.

The results from the multiple regressions performed on the data also show a distinct difference between the tests with and without ultraviolet light. The analysis on the data without ultraviolet light resulted in both the equation and the coefficients being statistically significant above the 1% level of significance. The data from tests without ultraviolet light indicate almost no statistical significance for the equation and little statistical significance for the coefficients. Again the equations were evaluated using the F-statistic and the coefficients using the t-statistic.

Applying an analysis of variance to the data resulted in all three factors having a significant effect on the removal process. The interaction analysis resulted in none of the interactions having a significant impact on the process. However the ozone and ultraviolet light interaction was very close to the critical value. This indicates that this interaction does have an effect on the



process, just not at the 5% level of significance.

#### Salicylic Acid

The results of the salicylic acid tests were puzzling. The fact that there were several instances where the non-purgeable carbon increased instead of decreasing. The plot of the lower concentration indicated good removal with ozone alone. However, after the addition of ultraviolet light the data did not respond as expected. The pH of the effluent was not measured and there is a possibility the  $pK_a$  of the acid was altered causing some unusual reactions to occur during the process. Since the salicylic acid was used as an indicator no further evaluation was considered.

## CHAPTER 6

### Summary

#### Conclusions

The general conclusion from the experiment is that the process of ozone and ultraviolet light in a counter current packed column demonstrates potential as a future technology for treatment of water supplies contaminated with trichloroethylene, toluene, and possibly other organic compounds. Although there were not enough data points to show stronger statistical correlation in all phases of the experiment, the results of the few data points available do show promise for the processes removal of contaminants. With more time and better sampling equipment, future experiments with this process will probably result in a proven technology to remove several pollutant compounds from water supplies, both surface and groundwater.

#### Recommendations

The next step is to test a larger scale model utilizing the data and results from this experiment. The larger model should be operated and tested at low G/L ratios and at an optimum ozone concentration. The optimum ozone concentration should result in the desired removal of a contaminant by the reaction of that contaminant with ozone and/or ultraviolet light. This influent ozone concentration should also result in a zero effluent concentration of ozone and minimize the contaminants

concentration in the air effluent.

The ozone should be measured at the influent and effluent ports of the column. This will allow for a mass balance calculation to be performed and closed on the entire process. In addition to measuring the ozone, in the case of chlorinated compounds, the chloride ion should be monitored in the water effluent. The effluent air should also be monitored and analyzed for the concentration of contaminant stripped from the liquid phase of the process. This will also help in determining the concentrations of the contaminant reacted with the ozone and/or ultraviolet light in the gas phase as opposed to the liquid phase.

The ultraviolet light wavelength should be selected to obtain the highest degree of removal of the contaminant from the water. The amount of light contacting the contaminated water will depend on the percentage of transmittance through the glass used in the design of the apparatus. The positioning of the lights should optimize the transmittance to achieve a high degree of penetration into the contaminated water. This could probably be achieved by placing the lights in quartz sleeves in the center of the column. Quartz provides the highest percentage of transmittance when compared to other photochemical equipment.

## Notes

<sup>1</sup> D. W. Sundstrom et al., "Destruction of Halogenated Aliphatics by Ultraviolet Catalyzed Oxidation with Hydrogen Peroxide," Hazardous Waste and Hazardous Materials, Vol. 3, no. 1 (1986): 101.

<sup>2</sup> Neil M. Ram et al., Significance and Treatment of Volatile Organic Compounds in Water Supplies (Michigan: Lewis, 1990), 313.

<sup>3</sup> Donald W. Sundstrom and Herbert E. Klei, "Destruction of Hazardous Wastes by Ultraviolet Catalyzed Oxidation," April 1983, University of Connecticut, Storrs: 2.

<sup>4</sup> Norma Lewis, "A Field Demonstration of the UV/Oxidation Technology to Treat Ground Water Contaminated with VOCs," Journal of the Air and Waste Management Association, Vol. 40, no. 4 (Apr. 1990): 540.

<sup>5</sup> William D. Bellamy et al., "Treatment of VOC-contaminated groundwater by hydrogen peroxide and ozone oxidatio," Research Journal WPCF, Vol. 63, no. 2 (mar/Apr 1991): 120.

<sup>6</sup> Harry M. Freeman, ed., Standard Handbook of Hazardous Treatment and Disposal, (New York: McGraw-Hill, 1989), 7.65.

<sup>7</sup> *ibid.*

<sup>8</sup> Barbara J. Marks and Mohindar Singh, "Comparison of Soil-gas, Soil, and Groundwater Contaminant Levels of Benzene and Toluene," Hazardous Materials Control, Nov/Dec 1990, 41.

<sup>9</sup> Neil M. Ram et al., Significance and Treatment of Volatile Organic Compounds in Water Supplies (Michigan: Lewis, 1990), 313-314.

<sup>10</sup> William D. Bellamy et al., "Treatment of VOC-contaminated groundwater by hydrogen peroxide and ozone oxidatio," Research Journal WPCF, Vol. 63, no. 2 (mar/Apr 1991): 120.

<sup>11</sup> William H. Glaze et al., "The Chemistry of Water Treatment Processes Involving Ozone, Hydrogen Peroxide and Ultraviolet Radiation," Ozone Science & Engineering, Vol. 9 (Sep 1987): 335.

<sup>12</sup> William D. Bellamy et al., "Treatment of VOC-contaminated groundwater by hydrogen peroxide and ozone oxidatio," Research Journal WPCF, Vol. 63, no. 2 (mar/Apr 1991): 121.

<sup>13</sup> Neil M. Ram et al., Significance and Treatment of Volatile Organic Compounds in Water Supplies (Michigan: Lewis, 1990), 343.

<sup>14</sup> William H. Glaze et al., "The Chemistry of Water Treatment Processes Involving Ozone, Hydrogen Peroxide and Ultraviolet Radiation," Ozone Science & Engineering, Vol. 9 (Sep 1987): 342-43.

<sup>15</sup> Neil M. Ram et al., Significance and Treatment of Volatile Organic Compounds in Water Supplies (Michigan: Lewis, 1990), 353.

<sup>16</sup> Welsbach Ozone Systems Corporation, Basic Manual of Applications and Laboratory Ozonation Techniques.

<sup>17</sup> W. Wesley Eckenfelder, Jr., Industrial Water Pollutuion Control, 2nd ed., (New York: McGraw-Hill, 1989), 136.

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